Simultaneous Removal of Hydrogen Sulfide and Organic Sulfur by Nickel Catalysts

Some work has been done at Morgantown with nickel catalysts for use in a manner similar to the Huff catalysts for simultaneous removal of hydrogen sulfide and organic sulfur. Data are not complete enough to report at this time.

Indications are that, while under certain conditions, results equal to the performance of the Huff catalysts can be obtained by nickel catalyst, difficulties are encountered with revivification. In most experiments, after catalyst pellets had absorbed a certain amount of sulfur, a silvery coating (evidently nickel) envelops the pellets, preventing subsequent revivification by air. Treating such pellets with acid does not evolve hydrogen sulfide until the pellets are broken, exposing the black, sulfided interior. One theory is that nickel sulfide, which is first formed, is reduced to metallic nickel by prolonged heating in a reducing atmosphere.

This theory is supported by results obtained from supported catalysts. Nickel on pumice, for example, if sulfided to the break point, was successfully revivified in some instances. In such cases no metallic coating was observed. Even such catalysts, however, if subjected to prolonged treatment by hot reducing gas (with or without hydrogen sulfide) behaved in a manner similar to the pelletted catalyst, and revivification could not be accomplished

In those experiments where revivification was obtained, virtually all of the sulfur was removed during the burn-off, very little being evolved during the first part of subsequent purification run. This difference from the behavior of the Huff catalysts makes further study of nickel catalyst desirable

Alkalized Iron for Removing Organic Sulfur

Alkalized iron was found to be successful for removing organic sulfur (except thiophene) from synthesis gas in German synthetic-liquid-fuel plants. For this reason, alkalized-iron treatment has been included in the purification train of the Bureau's demonstration plant at Louisiana, Mo. Its use in this plant is intended as a safety precaution to protect the Fischer-Tropsch catalyst in case of failure of the activated-carbon removal process which precedes the alkalized iron.

Actually, cost estimates prepared at Morgantown[33] indicate that the alkalized-iron process is much more expensive than removal by a relatively low cost activated carbon studied by the Bureau's Morgantown laboratory.

The high cost of alkalized-iron treatment of gas had led the Bureau to work on the development and investigation of other processes for removing organic sulfur. For this reason, only a limited amount of work has been done with alkalized iron, and that work has been chiefly in connection with selecting a suitable material for use in the demonstration plant.

One sample of material submitted by an American manufacturer was found to be much lower in alkali content than that used in the German practice. In Germany, alkalized iron generally contained 30 percent Na_2CO_3. The sample submitted to the Bureau contained only 1.2 percent alkali as Na_2CO_3.

Operating at 300 p.s.i.g., a temperature of 250° C., and a space velocity of 9,000 standard cu. ft. of gas per hour per cubic foot of catalyst, 25 grains of organic sulfur, as carbonyl sulfide, per 100 cu. ft. of gas were removed to a concentration below 0.1 grain per 100 cu. ft. of gas until the stoichiometrical amount of sulfur equivalent to the alkali content had been removed.

Further work on alkalized iron is in progress.

Removal of Organic Sulfur by Activated Carbon

A number of samples of activated carbon were tested for their ability to remove organic sulfur compounds from gas. Work was confined to the study of thiophene removal at atmospheric pressure and of carbonyl sulfide at 300 p.s.i.g.

Removal of Thiophene by Activated Carbon

Adsorption tests for thiophene removal were made on four Columbia carbons, CXA (4 x 6 pellets), SXA (6 x 8 pellets), SW (4 x 14 granules), and S (4 x 14 granules); three of the best carbons used by the Germans in their gas-purification systems, Supersorbon WS, SK, and TS (6 x 8 pellets); and one Pittsburgh Coke & Chemical Co. carbon, BP (4 x 14 granules).

By using 35 cc. of each carbon, bed depths of 6 inches were obtained. Later tests showed that, with some carbons, this bed depth is enough to give a true evaluation of a carbon's adsorptive capacity. Hydrogen, used as carrier gas, was bubbled through dibutyl phthalate containing the amount

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[33] Sands, A. E., and Schmidt, L. D., The Recovery of Sulfur from Synthesis Gas: Paper presented at 117th national meeting, Am. Chem. Soc., Houston, Tex., March 1950.

of thiophene necessary to give the hydrogen a sulfur content of 4 to 5 grains per 100 cu. ft. The thiophene content of the inlet and outlet gas was determined by the isatin method. The tests were run at room temperature and atmospheric pressure, using a space velocity of 400 hr.$^{-1}$.

The break point in these evaluation tests was considered to be 0.1 grain of sulfur per 100 cu. ft. of gas. When a carbon began passing this amount of thiophene, it was taken off stream.

The carbons were regenerated by steaming for 6 hours at 75 p.s.i.g., followed by drying in air for 2 hours at 105° C.

In all carbon evaluation tests, no attempt was made to determine attrition losses. Carbons were evaluated solely on their capacity for adsorbing the sulfur compound present in the gas. However, the volume and weight of each carbon were noted after each regeneration, and in no case did there appear to be any noticeable loss in carbon.

Table 14 summarizes the data obtained from the tests on the removal of thiophene.

TABLE 14. - Removal of thiophene with activated carbon

Space velocity: 400 hr.$^{-1}$
Inlet C_4H_4S concentration: 4-5 gr. S/100 cu. ft.

Carbon	No. of regenerations	S adsorbed, gram/gram C	Percent of original activity recovered
Columbia:			
CXA................	-	0.050	-
SXA................	-	.055	-
SW.................	-	.057	-
Columbia:			
CXA................	1	.034	68
SXA................	1	.042	76
SW.................	1	.049	86
Columbia:			
CXA................	2	.037	75
SXA................	2	.044	80
SW.................	2	.046	80
Supersorbon:			
WS.................	-	.035	-
SK.................	-	.044	-
TS.................	-	.032	-
Columbia:			
S..................	-	.070	-
Pittsburgh:			
BP.................	-	.051	-
Columbia:			
S..................	1	.066	94
Pittsburgh:			
BP.................	1	.043	85

The Supersorbon carbons exhibited the lowest initial adsorptive capacity; consequently, testing of these carbons was discontinued without any regenerations.

It should be noted that all of the remaining carbons lost some of their activity after the first regeneration. No further loss in activity, however, resulted after the second regeneration. The greater adsorptive capacity experienced in the first cycle is characteristic of adsorption in general and is supposed to represent a certain amount of carbon surface which retains the adsorbate so tenaciously that regeneration fails to remove the adsorbed impurity.

From the data presented in table 14, it can be seen that the Columbia S carbon displayed the greatest capacity for thiophene, adsorbing 6.6 percent of its weight in sulfur after one regeneration. The remaining carbons, with the exception of the CXA which had a somewhat lower capacity, adsorbed 4 to 5 percent of their weights.

Although no thiophene has been found in the synthesis gas produced in the Bureau's pilot plant, the removal of thiophene by activated carbon should be of interest wherever it might be desired to purify coke-oven gas which contains appreciable concentrations of thiophene. Because thiophene resists attack by catalytic conversion methods, adsorption by activated carbon is of special interest.

Removal of Carbonyl Sulfide by Activated Carbon

As more information became available from operation of the Bureau's gasification pilot plant at Morgantown and the Koppers gasifier at the Louisiana, Mo., Demonstration Plant, it became apparent that thiophene is not involved in the organic sulfur problem. Cost estimates for removing organic sulfur by means of alkalized iron indicated that such removal would be expensive, so it was desired to investigate the practicability of removing organic sulfur compounds (other than thiophene) by means of activated carbon. This work was undertaken, with special reference to the selection of a suitable carbon for use at the demonstration plant, where the alkalized-iron catalyst vessels are preceded by activated carbon drums.

While no determination of individual organic sulfur compounds (other than thiophene) has been made on the Bureau's synthesis gas, it is quite likely that carbonyl sulfide predominates. Activated carbon would not be expected to remove carbonyl sulfide as satisfactory as the other forms of organic sulfur compounds because carbonyl sulfide is a gas rather than a vapor. For these reasons, in the removal of organic sulfur from synthesis gas by activated carbon, the removal of carbonyl sulfide would be controlling, and therefore tests were made using this gas.

Since no commercial sources of pure carbonyl sulfide were available, it was necessary to prepare the compound. (It is understood that Matheson Co., Inc., will soon make carbonyl sulfide available in cylinders). Carbonyl sulfide was prepared in the Bureau's laboratory, using a method communicated to the authors by J. A. Shaw, Mellon Institute, Pittsburgh Pa.

According to this method, a saturated solution of potassium thiocyanate is reacted with 40-percent sulfuric acid. The evolved gases are bubbled through a 20-percent potassium hydroxide solution to remove any acid gases formed, followed by a 25-percent (by volume) solution of aniline in alcohol to remove carbon disulfide. The gas is then passed over ice chips to remove alcohol and water vapors, finally being collected in gas sample bottles over mercury. This method is slow and tedious but appears to be the best one for producing small amounts of pure carbonyl sulfide. A few bried experiments were tried whereby carbon monoxide was reacted with elemental sulfur at elevated temperatures but abandoned as being more uncertain and less convenient.

The carbonyl sulfide was displaced from the gas sample bottles, by means of mercury, into an evacuated gas cylinder. Pressure in the cylinder was then built up to 1,000 p.s.i.g., using hydrogen and nitrogen. Cylinders were allowed to stand several days to permit thorough mixing by diffusion.

Apparatus used for testing was fabricated from 1/2-inch extra-heavy pipe fittings and nipples. Gas flowed down through the carbon; 13 cc. of carbon was used as sample in each case, giving a bed depth of approximately 3 inches. For tests at higher velocities, glass wool was placed on top of the carbon to prevent lifting and entrainment.

The piping assembly provided for two samples of carbon to be run simultaneously, operating pressure being held at 300 p.s.i.g. by means of a pressure regulator on the cylinder. Throttling valves at the outlets of the carbons were provided, with pressure dropping to approximately atmospheric following these valves. Provision was made for sampling gas at the inlet and outlet of the carbons, sulfur content being determined by the platinum spiral method.

The two carbons tested under these conditions were Columbia S and Pittsburgh Coke & Chemical Co. BP. One run was made on a 3-inch bed depth and repeated using a 9-inch bed depth. For the two runs, fresh carbon was used in each case. The amounts of sulfur adsorbed to the break point (0.1 grain of sulfur per 100 cu. ft.) and to a point where only 25 percent of the inlet concentration was being removed were determined.

The latter point is designated as "total" and is of interest in applications where it is desired to only reduce the concentration of organic sulfur, with final removal being effected by some other means. This is the method of operation contemplated for the demonstration plant, where final removal is to be effected by alkalized iron.

The results obtained are shown in table 15. Increasing the bed depth from 3 inches to 9 inches greatly improved the capacity of the S carbon but had no appreciable effect (within the precision of the experiment) on the BP carbon. Because of this marked difference in effect of bed depth, further work with the 3-inch bed depth was abandoned.

In examining the results of subsequent cycles after the first, the BP carbon held its initial capacity but a very considerable loss in capacity was noted in the case of the S carbon.

TABLE 15. - Removal of carbonyl sulfide by activated carbon

Space velocity: 430 hr.$^{-1}$

Run No.	Inlet concentration gr. S/100 cu. ft.	3-inch bed S adsorbed, gram/gram C				9-inch bed S adsorbed, gram/gram C			
		Break point		Total		Break point		Total	
		BP	S	BP	S	BP	S	BP	S
1	29.2	0.012	0.021	0.016	0.038				
2	27.0					0.11	0.057	0.013	0.076
3	19.1					.018	.021	.019	.024
4	25.1					.013	.014	.014	.016

It was noted that, on drying the S carbon at 260° C. as part of the regeneration treatment, condensate from the effluent nitrogen contained considerable elemental sulfur. This did not happen with the BP carbon, nor was this observed with the S carbon when previously used for thiophene adsorption. It was later learned that the S carbon has an alkaline reaction, due to the presence of calcium salts, and it was concluded that carbonyl sulfide reacts with the alkali forming compounds not evolved by means of 75 p.s.i.g. steam. Heating to 260° C. apparently breaks down such compounds with the separation of elemental sulfur.

Presence of the alkali in the S carbon would account for the higher initial activity of the carbon and consumption of this alkali, together with probably incomplete removal of the elemental sulfur formed on decomposition, would account for the reduction in capacity in subsequent runs. This also explains the large drop in capacity between runs 1 and 2 compared with a small drop between runs 2 and 3.

In all regenerations of all carbons tested for carbonyl sulfide-removal ability, the presence of hydrogen sulfide and sulfur dioxide was noted in the effluent drying gas. Carrier gas, steam, and nitrogen used were tested and found to contain no oxygen. It is believed that oxygen may have been adsorbed from the air in handling the carbons, which could have reacted with some remaining carbonyl sulfide to produce sulfur dioxide at the higher temperature of drying. Moreover, it is conceivable that moisture could react with carbonyl sulfide at 260° C. to form both hydrogen sulfide and sulfur dioxide.

This evolution of hydrogen sulfide and sulfur dioxide will be significant if, in plant operation, purified synthesis gas, available at high temperatures, is used as drying gas, since the effluent drying gas would require purification before being used for synthesis.

Because of the regeneration difficulty experienced with the S carbon, which was attributed to the alkalinity, the manufacturer supplied a sample of carbon which had been treated to remove alkalinity. This carbon was identified as SA. Several tests on this carbon alone were carried out to determine whether regeneration difficulties had been eliminated. Data resulting from these tests are presented in table 16. These tests also employed 9-inch bed depths.

TABLE 16. - Data from tests of SA carbon

Run No.	Sp. vel., hr.$^{-1}$	Inlet COS concentration of S/100 cu. ft., gr.	S adsorbed, gram/gram C		Percent original activity recovered,
			To breakpoint	Total	
1	325	35.5	0.0342	0.0395	-
2	425	20.2	.0239	.0267	68
3	364	26.9	.0278	.0314	80
4	422	24.0	.0252	.0292	74
5	379	25.2	.0260	.0292	74

Although runs after the first show less sulfur adsorbed than in the initial run, the difference is believed to be due to lower inlet concentrations employed. It is significant that there is no progressive loss in capacity; to the contrary, results from runs 3, 4, and 5 show better capacities than that for run 2.

As the authors were satisfied that the regeneration difficulties experienced with the alkaline S carbon had been eliminated with the use of the alkali-free SA carbon, work was resumed on the comparison with the BP carbon. All previous tests had utilized a carrier gas that was free of carbon dioxide. It was now decided that, for evaluation purposes, carbon to be used on synthesis gas should contain a concentration of carbon dioxide corresponding to that of synthesis gas. A series of tests with varying carbon dioxide concentrations in the inlet gas was then carried out. Results of these tests will be found in table 17.

These tests show that carbon dioxide has a marked effect on the capacity of activated carbons for carbonyl sulfide adsorption. Moreover, this effect is more pronounced with the SA than with the BP carbon, resulting in improved relative capacity for the BP carbon when carbon dioxide is present in the gas. Thus, when the gas contains no carbon dioxide, the test showed that the relative capacity of the BP carbon was 48.4 percent of the capacity of the SA carbon, while with 37 percent carbon dioxide in the gas, the relative capacity of the BP carbon was increased to 97.2 percent.

Unfortunately in this series of tests, the gas used in two of the runs (2 and 4) varied considerably in carbonyl sulfide concentration, owing to the use of cylinders that had not stood long enough to obtain uniform mixing of the carbonyl sulfide with the carrier gas. This did not invalidate the series of tests as a whole, however.

The improved relative performance of the BP carbon when carbon dioxide is present in the gas - as will be the case in synthesis gas - is of considerable importance. Although the SA carbon is still superior in adsorptive capacity to the BP, an appreciable difference in the price for the two carbons made further consideration of the BP carbon necessary. The SA carbon, an excellent grade of cocoanut-shell carbon, sells for around $1.10 per pound in large quantities, while the BP carbon, which is made from coal, sells for 35 cents per pound.

TABLE 17. - Tests at varying concentrations of CO_2

Run No.	Carbon	Sp. vel., hr.$^{-1}$	CO_2 in gas, percent	Inlet COS concentration, gr. S/100 cu. ft.	S adsorbed, gram/gram C		Relative capacity of BP, percent
					Break point	Total	
1	SA	325	0	35.5	0.0342	0.0395	48.4
	BP	352	0	35.5	.0155	.0191	
2	SA	284	7.1	9.5-55	.0060	.0136	
	BP	276	7.1	9.5-55	.0034	.0091	67.0
3	SA	387	15.8	32.5	.0069	.0108	
	BP	338	15.8	32.5	.0042	.0075	68.5
4	SA	326	33.0	25-31	.0026	.0053	
	BP	365	33.0	25-31	.0009	.0041	77.4
5	SA	464	37.0	38	.0010	.0035	
	BP	368	37.0	38	.0017	.0034	97.2
6	SA	322	18.1	34.5	.0067	.0120	
	BP	393	18.1	34.5	-	.0074	61.6

Consequently, a new series of tests was run, keeping the carbon dioxide and carbonyl sulfide concentrations as nearly constant as possible, and at values approximating those for synthesis gas. Table 18 shows the results obtained. It will be noted that these results show a somewhat higher relative capacity for the BP carbon than was obtained from Run 4 of table 17 which was the nearest approximation to the conditions of the present series of tests. No explanation is available for this difference, unless there was a difference in the degree of regeneration obtained.

TABLE 18. - Additional tests of BP and SA carbons

Run No.	Carbon	Operating pressure, p.s.i.g.	Sp. vel., hr.$^{-1}$	CO_2 in gas, percent	Inlet COS concentration, gr. S/100 cu. ft.	S adsorbed, gram/gram C		Relative capacity of BP, percent
						Break point	Total	
1	SA	300	291	16.3	26.0	0.0069	0.0100	
	BP	300	341	16.3	26.0	.0047	.0084	84.0
2	SA	300	314	15.8	25.0	.0050	.0083	
	BP	300	302	15.8	25.0	.0041	.0071	85.0
3	SA	300	406	17.8	22.7	.0045	.0071	
	BP	300	371	17.8	22.7	.0036	.0057	80.3
4	SA	300	498	13.2	32.5	.0062	.0143	
	BP	300	368	13.2	32.5	.0068	.0124	86.8
5	SA	0	348	15.7	19.6	.0018	.0029	
	BP	0	314	15.4	19.6	.0013	.0018	62.2
6	SA	0	314	15.7	36.2	.0021	.0039	
	BP	0	310	15.4	36.2	.0017	.0026	66.7

The four runs (at 300 p.s.i.g.) shown in table 18, however, show good reproducibility and are believed to be reliable. The relative capacities for the BP carbon range from 80.3 to 86.8 percent, a narrow range considering inevitable differences in gas composition and probably in effectiveness of regeneration.

Runs 5 and 6 of table 18 were operated at atmospheric pressure, to show the effect of pressure on the adsorption process. Capacity (either to the break point or the 25 percent removal point) is increased in the order of 3 or 4 times by increasing the pressure from 1 to 21 atmospheres absolute.

In all of the preceding tests using 9-inch-bed depths, space velocities at standard conditions had been held to 300 to 400 and corresponding linear velocities approximately 10 ft. per hour (at flow conditions). It was now desired to run tests at linear velocities more nearly comparable to plant conditions at the demonstration plant. Accordingly, tests were carried out on SA and BP carbons at a linear velocity (flow conditions) of 500 ft. per hour and higher. To prolong the test sufficiently to obtain data, the bed depth was increased to 3 feet.

At the same time, to obtain the high velocities desired without consuming a prohibitive amount of cylinder gas, the diameter of the beds was decreased. For those tests, the carbon was contained in 3/8-inch extra-heavy pipes, instead of 1/2-inch size as heretofore. To reduce edge effect in the smaller pipe, carbon was ground to 16- by 20-mesh. With this size of carbon, it was possible to have at least 8 granules of carbon across the diameter of the pipe.

A comparison was first made between the 3-feet and 9-inch bed depths at the previous velocity used, that is, 10 feet per hour, using BP carbon in both beds. The purpose of this test was to determine the effect of bed depth. Using the same gas (28.0 percent CO_2 and 22.5 grains sulfur per 100 cu. ft.), the 9-inch bed showed a capacity of 0.0045 gram of sulfur per gram of carbon and the 3-foot bed a capacity of 0.0042 gram per gram. These results validated the results obtained with 9-inch bed depths, since no appreciable difference in result was obtained between the 9-inch and 3-foot depths.

Next, BP and SA carbons were compared, using a 3-foot bed depth and a linear velocity of approximately 500 feet per hour. Table 19 gives the results of these tests.

TABLE 19. - Tests comparing carbons BP and SA

Run No.	Carbon	Sp. vel., hr.$^{-1}$	Linear vel., ft./hr.	CO_2 in gas, percent	Inlet COS concentration, gr. S/100 cu. ft.	S adsorbed, gram/gram C	
						Break point	Total
1	BP	3,590	510	17.5	32.1	0.0060	0.0078
2	BP	3,560	505	18.0	32.1	.0055	.0078
3	SA	3,500	469	14.4	30.3	.0075	.0110
4	SA	3,720	500	18.0	27.5	.0074	.0107

It is observed that each carbon exhibits substantially the same adsorptive capacity under the new condition of greater bed depth and higher velocity as it did when tested at the lower velocity and using a shallower bed depth.

At this time, Pittsburgh Coke & Chemical Co. supplied a new sample of carbon (GW) which was quoted at 15 cents per pound, and no further work was done with either the BP or SA carbons.

Table 20 gives data from a series of runs made on carbon, in which the carbon dioxide content was varied from 0 to 34.5 percent and the carbonyl sulfide concentration was varied from 5.1 to 48.6 grains of sulfur per 100 cu. ft. These data are graphically presented in figure 17. Comparing these data with those previously presented for BP carbon, it is evident that the performance of the GW carbon is substantially the same as that of the BP. The effect of carbon dioxide on the performance of the GW carbon is similar to that experienced with the BP carbon.

TABLE 20. - Results of tests on carbon GW

Run No.	Sp. vel., hr.$^{-1}$	Linear vel., ft./hr.	CO_2 in gas, percent	Inlet COS concentration, gr. S/100 cu. ft.	S adsorbed, gram/gram C	
					Break point	Total
1	4,210	492	15.6	22.8	0.0041	0.0058
2	4,110	486	17.9	30.8	.0056	.0075
3	4,050	468	17.9	27.3	.0050	.0069
4	3,950	450	16.7	48.6	.0083	.0111
5	4,470	498	16.5	21.8	.0055	.0075
6	4,650	500	9.1	7.0	.0018	.0024
7	4,140	430	34.5	23.6	.0021	.0034
8	4,700	484	0	20.0	.0195	.0212
9	4,350	432	16.0	12.5	.0026	.0036
10	4,270	425	18.7	9.7	.0016	.0022
11	770	77	19.7	10.0	.0036	.0066
12	992	97	19.7	18.6	.0040	.0055
13	1,010	94	16.3	32.6	.0063	.0079
14	9,570	1,083	14.1	23.1	.0048	.0064
15	9,520	1,060	0	24.9	.0229	.0259
16	21,500	2,170	0	22.9	.0244	.0274
17	18,600	1,960	10.8	22.4	.0059	.0078
18	18,600	2,020	11.3	25.9	.0071	.0096

In carrying out the tests, results of which are presented in table 20 and figure 17, it was noted that in run 6, where the inlet organic sulfur content was 7 grains per 100 cu. ft., the carbon reached the break-point at about the same time as in those runs where the organic sulfur content was as high as 30 grains per 100 cu. ft.

Because of this observation, more tests were run in which the organic sulfur content of the gas to be treated was varied. These tests proved that the service time of the carbon to the break-point is the same within limits of organic sulfur content between 10 and 30 grains per 100 cu. ft. when the

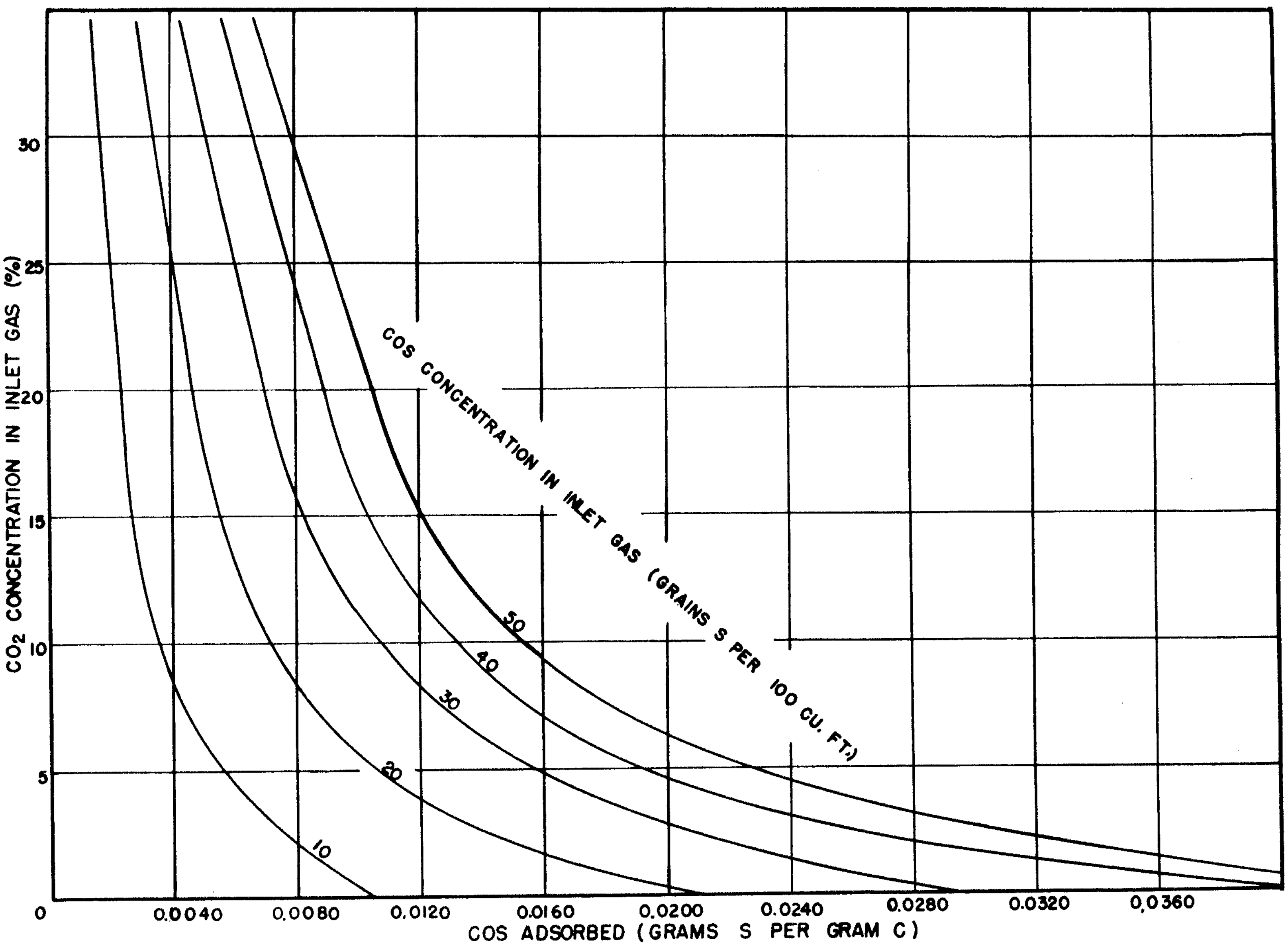

Figure 17. - Adsorptive capacity of GW carbon for COS in H_2-CO_2 mixtures, linear velocity 500-2,000 feet per hour at 300 p.s.i.g.

linear velocity is between 500 and 2,000 feet per hour. (The 2,000 linear velocity corresponds to a space velocity of 21,000 $hr.^{-1}$). For concentrations above 30 grains per 100 cu. ft., and also when the velocity is lowered to 76 feet per hour, the service time is affected by changes in concentration and velocity.

The lack of dependence of service time (within limits) on concentration of organic sulfur was next confirmed with BP and SA carbons. Data from one run follow:

Run No.	Carbon used	Sp. vel., hr.	Linear vel., ft./hr.	CO_2 in gas,	Inlet COS conc. S/100 cu. ft., gr.	S adsorbed, gram/gram C, Break point	Total
1	BP	3820	496	15.9	12.5	0.0025	0.0031
1	SA	4170	432	15.9	12.5	.0037	.0050

Comparison of these data with those previously presented shows that reducing the organic sulfur to one-half the former value did not change the service time.

The fact that the service time of the carbons is the same for inlet organic sulfur concentrations between 10 and 30 grains per 100 cu. ft. is important, since it points to the fact that, if the active carbon is used for removing organic sulfur, the removal cost does not change (within the limits indicated) for changing organic sulfur concentrations. Service time - that is, the length of the adsorption period in the cycle - is the determining factor in cost of removal, since this determines the size of vessels used and the amount of steam required for regeneration.

Since the cost of organic sulfur removal by means of activated carbon does not change for concentrations between 10 and 30 grains per 100 cu. ft., it means that coals having sulfur contents between 1.0 and 5.0 percent can be used with no effect on cost of organic sulfur removal, providing that the steam:coal ratio is controlled (as can be done) to keep the organic sulfur content within the limits specified.

In another paper by one of the authors of this report[34], a cost estimate for gas purification in a 10,000-barrel-per-day liquid-fuel plant (treating 336,000,000 cu. ft. of raw gas per day), indicates that with sulfur recovery by the Claus kiln process, the cost of removal of hydrogen sulfide decreases with increasing sulfur in the coal. The same estimate shows that, if only 0.1 percent of the carbon life is lost (due to carbon degradation) per cycle, the total cost of organic sulfur removal by means of activated carbon using GW carbon would be 0.216 cent per 1,000 cu. ft. This cost, under conditions already stated, would remain constant for coal-sulfur content between 1 and 5 percent.

Thus, it appears that the cost of total sulfur removal in the hypothetical plant cited would decrease from a figure of about 1.0 cent per 1,000 cu. ft.

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[34] See footnote 33.

when the coal sulfur content is 1 percent to a cost of about 0.6 cent per 1,000 fu. ft. when the sulfur content of the coal is 5 percent.

It should be noted that these costs are predicated on the following conditions:

1. Credit for recovered sulfur at $18.00 per ton, less costs for conversion of hydrogen sulfide to elemental sulfur.

2. Plant capacity 336,000,000 cu. ft. per day.

3. Assumption that plant operating results with activated carbon duplicate laboratory results.

Cost estimates at this stage should be considered as tentative only. One of the prime functions of the Bureau's demonstration plant is to determine costs. With demonstration plant operations on a scale larger than the usual pilot plant, there will be an excellent opportunity to obtain reliable cost data.

Morgantown Gas-Purification Pilot Plant

Because bench-scale experiments in the laboratory are not always adequate to evaluate processes, and because the size and other requirements of the demonstration plant preclude its use for the study of a large number of of different processes of gas purification independently of the other uses for the demonstration plant, the intermediate pilot-plant scale is necessary to evaluate processes that eventually will find their way into the demonstration plant.

In cooperation with the Gas Processes Division of the Girdler Corp., a gas-purification pilot plant was designed. Component parts of the plant were supplied by Girdler, the assembly and erection being carried out by the Morgantown Station's mechanical section.

This pilot plant includes an adsorber and reactivator for the Girbotol process, iron oxide towers, activated-carbon drums, gas heater, hot catalyst vessel, and the necessary pumps, piping, and instrumentation. A flow sheet of the plant is given in figure 18, and a photograph of the plant is shown as figure 19.

It should be noted that, while the absorber and reactivator were designed for the Girbotol process, this equipment can be used, with little or no modification, to study other processes and will be so used. In general, the equipment can be used for studying any process in which hydrogen sulfide is removed by absorption with reactivation of the fouled absorbent accomplished by the use of steam. These processes, in addition to the Girbotol process, include the Fluor process, Koppers vacuum carbonate process, Shell phosphate process, and others.

Similarly, the hot catalyst vessel was supplied for studying the Girdler organic sulfur conversion catalyst. For this use, the catalyst would be first

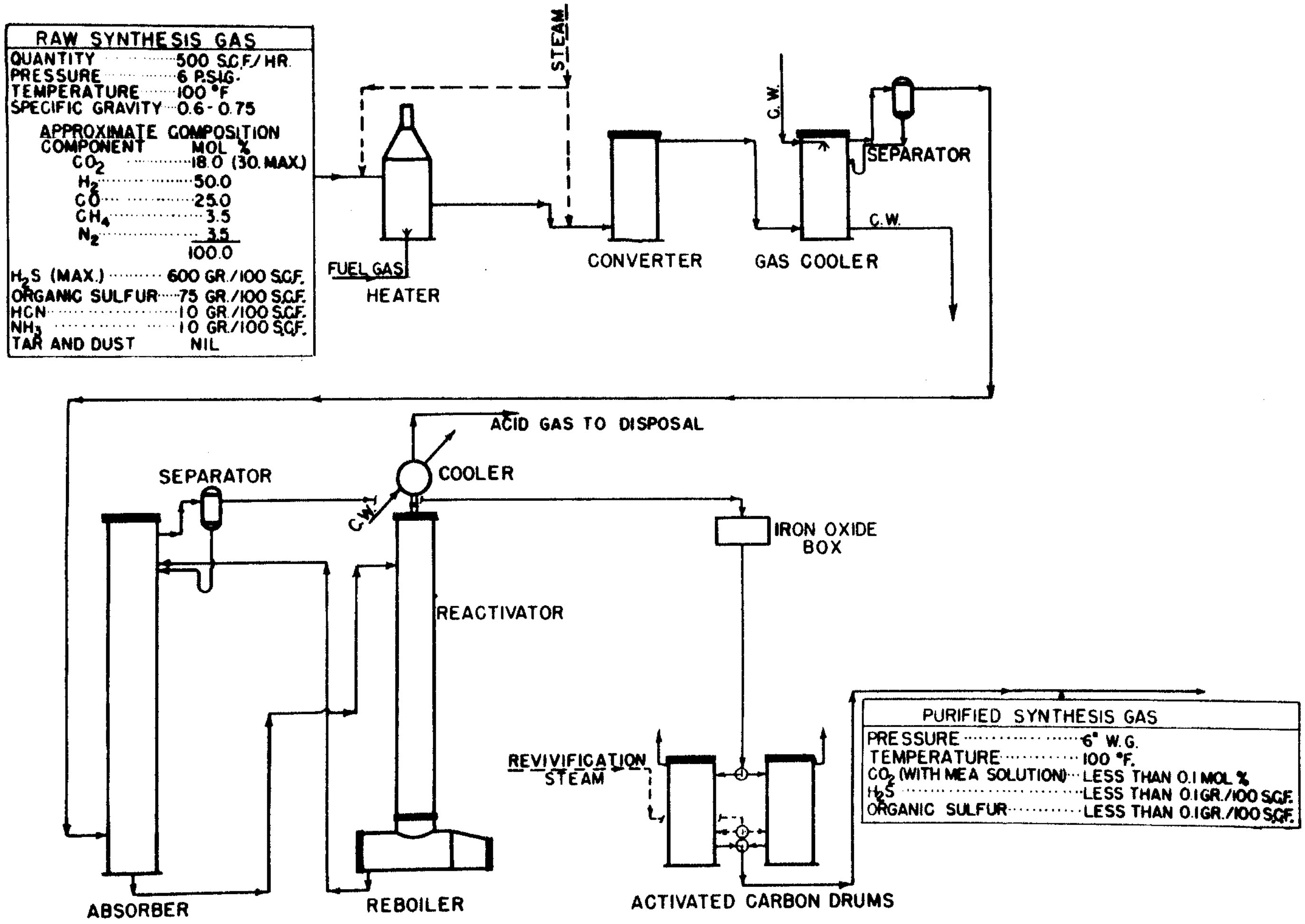

Figure 18. - 500 s.c.f.h. synthesis-gas-purification pilot plant.

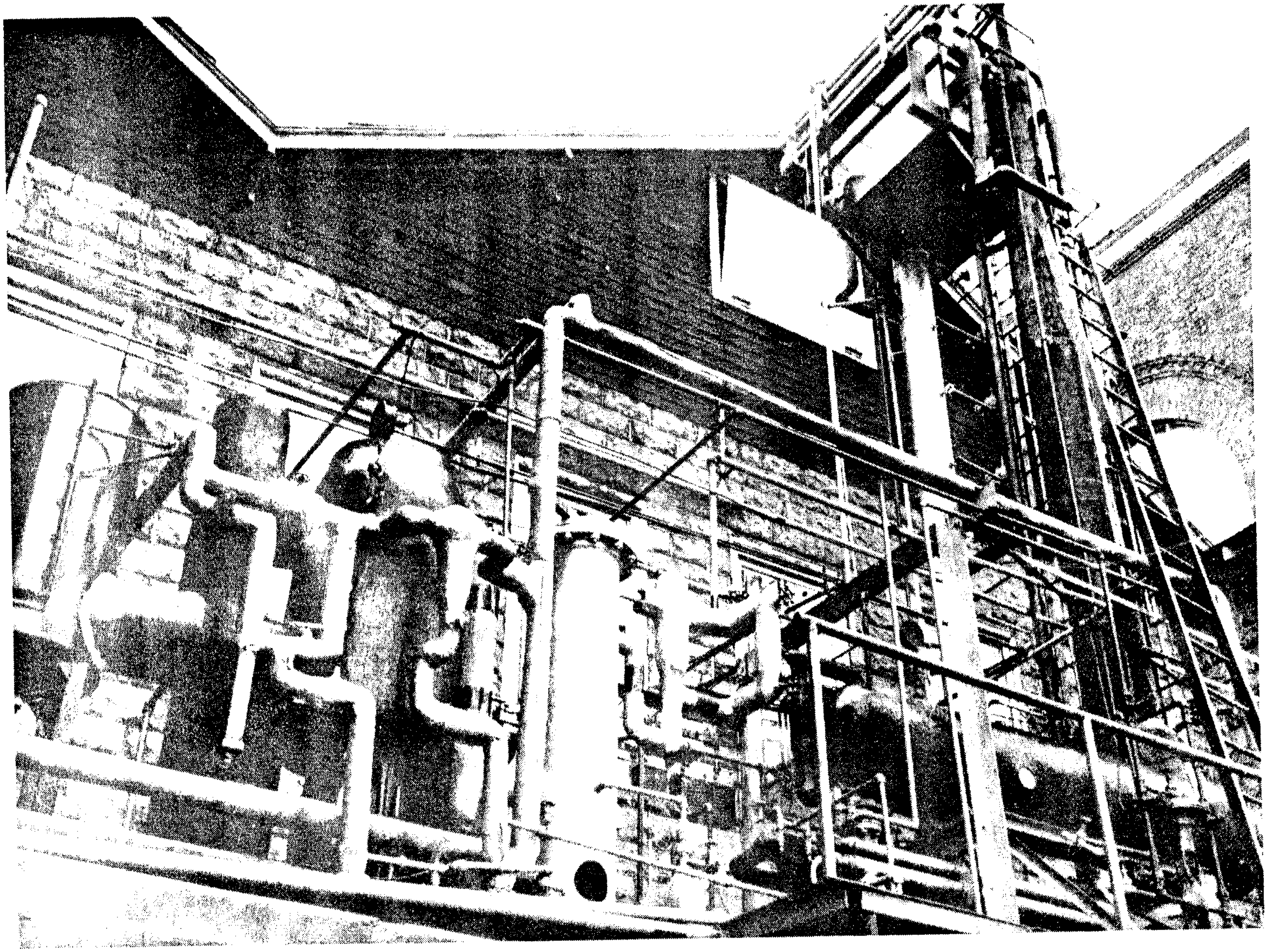

Figure 19. - View of gas-purification pilot plant.

in series. Piping and valves are so arranged as to permit use of the hot catalyst vessel at the end of the train, where it might be used for alkalized-iron catalyst. Various possible combinations are possible. For example, Huff catalyst could be used as the single method of treatment to remove all of the organic sulfur and hydrogen sulfide (probably requiring an additional catalyst vessel). In this case the hydrogen sulfide scrubbing and iron oxide steps would not be used. Or, the Huff catalyst could follow the scrubbing step, in which case residual hydrogen sulfide and organic sulfur would be removed by the Huff catalyst.

The pilot plant was originally designed for 500 cu. ft. per hour and a pressure of 6 p.s.i.g. The plant has been modified, however, to permit operation of all but the hot catalyst vessel at 300 p.s.i.g. Under this pressure, it is assumed that a gas capacity approaching 10,000 cu. ft. per hour can be treated.

Figure 18 gives some design data and the flow system followed when the organic sulfur catalyst is used. As has been previously stated, laboratory investigations showed that the low organic sulfur value of 0.1 grain per 100 cu. ft. cannot be obtained directly from the use of the Girdler catalyst, although this is indicated on the diagram.

When the Girdler catalyst is used, the flow can be traced by referring to figure 18. Raw gas containing up to 600 grains of hydrogen sulfide and 75 grains of organic sulfur per 100 cu. ft. enters the gas heater, is heated to 400° C., and passes to the converter where organic sulfur is largely converted to hydrogen sulfide. The gas then passes through the gas cooler, where the gas passes up through 1/2-inch Raschig rings and is cooled by a water wash. The gas then passes on to the Raschig-ring-packed absorber, where the gas is scrubbed counter-currently with 50 percent triethanolamine solution. Leaving the top of the absorber, the gas next flows through one to three iron oxide towers where the remaining (perhaps 25 grains per 100 cu. ft.) hydrogen sulfide is removed. The gas then flows through one of the two activated-carbon drums, where any residual organic sulfur compounds or other miscellaneous impurities, such as gum-forming hydrocarbons, are removed. The purified gas is then metered.

The gas-heater and hot catalyst vessel have not been converted to 300 p.s.i.g., because the heat duty of the heater is not sufficient to supply the heat required when the gas flow is increased nearly twenty-fold, as is the case in increasing the pressure from atmospheric pressure to 300 p.s.i.g.

This vessel can be used at gas rates of 500 cu. ft. per hour (atmospheric pressure). When it is desired to operate at 300 p.s.i.g. and use hot catalyst, it will be necessary to supply two new vessels and a higher-capacity gas heater. The present gas heater can then be used for heating regeneration air for the Huff catalyst when that process is studied.

The gas-purification pilot plant will have considerable flexibility and will permit effective study of new processes developed or modified in the Bureau's laboratory. The study of commercial processes, their relative evaluation, and their applicability to the special requirements of synthesis-gas purification can also be undertaken.

It is believed that, with concurrent investigations made in the laboratory and pilot plant, definite contributions to the art of gas purification can be made, not only for the resultant advantage to the synthetic liquid-fuels program, but in the interest of the gas industry generally.