

INTRODUCTION

This report deals with a portion of the research and development work in the field of synthesis gas purification, carried out by the Bureau of Mines at its Morgantown, W. Va., Station in cooperation with West Virginia University.

The Bureau's work in connection with gas purification has been performed with the objective of finding effective, low-cost, processes for removing impurities from synthesis gas to protect the catalyst used in the Fischer-Tropsch process for production of liquid fuels.^{3/} Synthesis gas used for the production of other chemicals, such as ammonia, alcohols, and methane, requires equally rigorous purification. Although present-day practice in the manufactured-gas industry does not require such a high degree of purification, there is increasing interest in the complete removal of sulfur compounds from city gas.

Although the gas-purification work at Morgantown deals with several impurities, major effort has been devoted to organic sulfur compounds in gas; this paper represents a progress report on some of the more important studies in connection with those compounds. Because this is a progress report on the Bureau's experimental work, no attempt has been made to cover the work of others on the subject; references to the literature have been restricted to those bearing directly on the work described.

SUMMARY AND CONCLUSIONS

1. Most of the conclusions reached in this report - except those bearing on analytical methods - should be considered tentative only, because investigations on the occurrence and removal of organic sulfur are continuing.
2. No thiophene has been found in synthesis gas made from pulverized coal, steam, and oxygen in the Bureau's pilot plants.
3. Addition of 0.038 pound of hydrated lime per pound of coal lowered the organic sulfur content of the gas but had no effect on hydrogen sulfide content; doubling this ratio of lime to coal further reduced the concentration of organic sulfur and reduced the concentration of hydrogen sulfide in the gas.
4. The relation between sulfur content of coal and organic sulfur concentration in the gas cannot be simply stated. This relationship varies with rank of the coal, steam:coal ratio, and other operating

^{3/} Sands, A. E., Wainwright, H. W., and Schmidt, L. D., Purification of Synthesis Gas Produced from Pulverized Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 607-620.

conditions. Typical concentrations of organic sulfur in the gas for different operating conditions are presented.

5. Other conditions remaining unchanged, increasing the steam to coal ratio greatly decreases the organic sulfur concentration in the gas.

6. Different combustion methods for determination of total (organic) sulfur are presented. Of these, the I.G.T. method, with modifications by the Bureau's laboratory, appears to be the best.

7. A limited amount of work on the modification of the Referees' method for determination of total (organic) sulfur shows that the method, as modified, can give excellent results.

8. A procedure using the Betz-Hellige turbidimeter for determining barium sulfate resulting from combustion methods of determining total (organic) sulfur is presented. This procedure, as revised by the Bureau's laboratory, can determine as little as 0.0001 grain of sulfur (as barium sulfate) per 250 ml. of solution.

9. A procedure for the turbidimetric determination of barium sulfate using the Beckman spectrophotometer, is outlined. As little as 0.001 grain of sulfur (as barium sulfate) per 250 ml. of solution can be determined. Although this method has only one-tenth the sensitivity of the Betz-Hellige method, concentration of solutions by evaporation can overcome this objection. Elimination of the necessity of judging light-intensity end points is the great advantage of this method.

10. Other methods for determining small amounts of sulfate were investigated but found to have no advantages compared with turbidimetric methods.

11. Difficulties were experienced in obtaining satisfactory results from a method for organic sulfur determination which depends on conversion of organic sulfur to hydrogen sulfide over activated alumina. Although the difficulties can undoubtedly be eliminated, further investigation of the method was dropped because of the advantages of the platinum spiral method.

12. The analytical method of Lusby, involving conversion of organic sulfur to hydrogen sulfide, utilizing the hydrogen content of the gas and a hot platinum spiral as catalyst, was studied and further developed. This method has been adopted by the Bureau's laboratory because of its sensitivity, accuracy, and speed. Details of the method are presented.

13. A method for catalytic conversion of organic sulfur in the presence of large amounts of hydrogen sulfide was studied as a process for purification. Due to an equilibrium between hydrogen sulfide, carbon monoxide, and organic sulfur (presumably carbonyl sulfide), the method cannot be used in its present form for the complete elimination of organic sulfur from synthesis gas. The method probably has considerable merit for certain applications where about 2 grains of organic sulfur can be tolerated in the purified gas.

14. Brief studies of the use of cobalt molybdate and of platinum on activated alumina for use as catalysts in organic sulfur elimination did not give satisfactory results.

15. Experiments with catalysts which simultaneously remove organic sulfur and hydrogen sulfide (Huff catalysts) gave excellent results. Purification can be effected to leave less than 0.1 grain of total sulfur per 100 cu. ft. of purified gas. Further work on this method is in progress.

16. A limited amount of investigation of alkalized-iron catalyst for the oxidation and removal of organic sulfur, as used in German synthetic fuel plants, proved that the catalyst produced by an American manufacturer can be used for purification of synthesis gas to below 0.1 grain of total sulfur per 100 cu. ft. The method is believed to be more expensive than some other possible methods. Further work with this method is in progress.

17. Several activated carbon samples were evaluated for their ability to remove thiophene at atmospheric pressure. In most cases, the carbons adsorbed 4 to 5 percent of their weights in sulfur (as thiophene). Data are presented.

18. The removal of carbonyl sulfide at 300 p.s.i.g. by activated carbon was studied. Capacities of carbons were lowered by carbon dioxide in the gas. Data on the effect of linear velocity, carbonyl concentration, and carbon dioxide concentration on capacity are presented.

19. The Bureau's gas-purification pilot plant is described.

ACKNOWLEDGMENTS

The work covered in this report represents contributions by virtually the entire Gas Treating and Testing Section at the Morgantown Station. These members of the personnel have included a large number of West Virginia University student part-time employees over a period of time.

In addition to contributions by the Morgantown staff, it is desired to make special acknowledgment to Dr. W. J. Huff, chairman of the Chemical Engineering Department of the University of Maryland and special consultant to the Bureau of Mines. Dr. Huff has closely followed the work at Morgantown and in consultation with the Morgantown staff has been most helpful in offering practical suggestions, contributing pertinent data out of his wide experience in gas purification, and offering encouragement in the work. The work on the Huff catalyst in this report is, of course, continuation of earlier work by him.

Special acknowledgment is made to Dr. R. G. Dressler and H. R. Batchelder of the Bureau's Demonstration Plant at Louisiana, Mo., for many helpful suggestions in planning the purification program. Work on active carbon especially was carried out to supply information requested by H. R. Batchelder.

Assistance rendered by Dr. R. E. Reitmeier, Director of Research and Development of the Gas Processes Division, The Girdler Corp., is also

gratefully acknowledged. Dr. Reitmeier's cooperation and that of his associates in making data available, supplying catalyst samples, offering many helpful suggestions, and in assisting in the design of the Bureau's gas-purification pilot plant are deeply appreciated.

OCCURRENCE OF ORGANIC SULFUR

Two pilot plants for the production of synthesis gas directly from pulverized coal, steam, and oxygen have been operated at Morgantown. These plants have been fully described in other Reports of Investigations.^{4/5/} Briefly stated, the operation of these two pilot plants differs primarily in the proportioning of steam and coal.

The larger pilot plant (capacity, 500 lb. of coal per hour) has used steam:coal ratios ranging from 0.19 to 3.43 lb. of steam per pound of coal. The smaller pilot plant (capacity, 50 lb. of coal per hour) uses a large excess of coal to steam - in many instances using no steam except that formed from the water content of the coal. Thus, steam:coal ratios as low as 0.01 lb. of steam per pound of coal were employed.

Before these pilot plants were put into operation, some concern was felt with respect to the concentrations and types of organic sulfur compounds that might be obtained. Earlier bench-scale experiments in the laboratory - together with German synthetic liquid fuel-plant operating data - revealed that carbonyl sulfide (COS), carbon disulfide (CS₂), and mercaptans (R-SH) can be removed effectively by certain catalytic processes and that it is immaterial which of these types may be present. Thiophene (C₄H₄S), on the other hand, resists catalytic treatment, whether by hydrogenation, hydrolysis, or oxidation, and the presence of thiophene in the gas would require special treatment.

It was known that coke-over gas, as well as gas made from pulverized coal in one German plant (Wintershall-Schmalfeldt),^{6/} contained thiophene, and it was believed that gas made in the Morgantown pilot plants might similarly yield thiophene. One research project in the Bureau's laboratory studied the pyrolysis of thiophene. In this work a concentration of 2,000 grains of sulfur as thiophene per 100 cu. ft. of gas was employed. It was found that, in an atmosphere of hydrogen at a temperature as low as 955° C. and a contact time of 0.006 hour, at least 95 percent of the thiophene content of the gas mixture was decomposed to hydrogen sulfide. The remaining 5 percent of thiophene apparently was converted to carbon disulfide.

-
- ^{4/} Strimbeck, G. R., Holden, John H., Rockenbach, L. P., Cordiner, J. B. and Schmidt, L. D., The Morgantown Pilot Plant Gasification of Pulverized Coal with Oxygen and Highly Superheated Steam: Bureau of Mines Rept. of Investigations (in preparation).
- ^{5/} Sebastian, J. J. S., Edeburn, P. W., Bonar, F., Bonifield, L. W., and Schmidt, L. D., Laboratory-Scale Work on Synthesis-Gas Production: Bureau of Mines Rept. of Investigations (in preparation).
- ^{6/} Morley, R. J., The Wintershall-Schmalfeldt Process for the Manufacture of Synthesis Gas at Lutzendorf: British Intelligence Objectives Subcommittee Final Report 1142, Item 30.

In an atmosphere of nitrogen, under similar conditions, 42 percent of the thiophene content was converted to hydrogen sulfide, the remainder being converted to carbon disulfide. In this case, increasing temperature lowered the conversion to hydrogen sulfide and correspondingly increased the carbon disulfide content.

Information from O. Hubmann, formerly technical director and chief engineer, Lurgi Co., Frankfort, Germany, in 1947, had indicated that a temperature perhaps as high as 1,200° C. (without a catalyst) would be required to convert thiophene completely to hydrogen sulfide. Results in the Bureau's pilot plants confirmed the laboratory results, since, at temperatures as low as 982° C., no thiophene could be found by the isatin test.

No attempts have been made to determine the other types of organic sulfur compounds in gas made in the pilot plants separately since - as has been stated - except for thiophene, the form of organic sulfur is unimportant in catalytic-removal processes.

Organic Sulfur Contents of Gas Produced

Tables 1 and 2 give the sulfur contents of gas made in the small gasifier; table 3 gives similar data for the large gasifier. Several conclusions may be drawn from examination of these data. The relation between organic sulfur concentration in the gas and sulfur content of the coal appears to be affected by the steam:coal ratio and the type of coal gasified. It will be noted that, with a given coal, generally lower organic sulfur concentrations result from higher steam:coal ratios. This is undoubtedly due to hydrolysis and destructive hydrogenation of the organic sulfur compounds; more excess steam and higher hydrogen contents are present in these cases.

TABLE 1. - Sulfur in gas from 50-lb. gasifier

Coal used	S in coal, percent	Steam:coal ratio	H ₂ in gas, percent	Generator temp., °F.	Grains/100 cu. ft.	
					H ₂ S	Org. S
West Virginia						
bituminous.....	2.9	0.23	33.3	1,997	310	43.9
Do.....	2.9	.08	35.0	1,927	330	50.6
Colorado subbituminous.	.4	.18	33.8	1,810	60	5.3
Pennsylvania anthracite	.9	.17	31.0	1,820	110	23.8
Do.....	.9	.29	34.9	1,800	100	21.2

TABLE 2. - Sulfur in gas from coal-lime runs (50-lb. gasifier)

Coal used	S in coal, percent	Steam:coal ratio	Lime:ash ratio	H ₂ in gas, percent	Generator temp., °F.	Grains/100 cu. ft.	
						H ₂ S	Org. S
West Virginia bituminous..	2.8	0.01	-	32.2	1,891	275	43.4
Do.....	2.8	.01	0.35	32.8	1,853	295	25.7
Do.....	2.8	.01	.70	31.9	1,845	80	5.1

TABLE 3. - Sulfur in gas from 500-lb. gasifier

Coal used	S in coal, percent	Steam:coal ratio	H ₂ in gas, percent	Generator Temp., °F.	Grains/100 cu. ft.	
					H ₂ S	Org. S
West Virginia bituminous.....	2.9	2.71	48.7	2,296	327	11.5
Do.....	2.9	2.08	52.7	2,172	313	14.4
Do.....	2.9	2.05	49.0	2,150	317	13.4
Do.....	2.4	.92	36.3	2,115	335	28.3
Do.....	2.4	1.12	37.4	2,238	290	19.6
Do.....	2.4	.59	36.4	2,311	376	24.0
Do.....	2.4	.43	32.3	2,358	358	30.1
Do.....	2.4	.40	36.3	2,230	365	30.5
Do.....	2.4	.38	35.1	2,310	390	26.2
Do.....	2.0	1.28	39.7	2,375	300	21.6
Wyoming bituminous..	1.1	1.10	39.1	2,536	150	19.0
Do.....	1.1	1.08	37.7	2,468	157	21.4
Do.....	1.1	1.10	37.1	2,498	163	18.8

On the basis of two runs with anthracite, it would appear that this coal (compared with Sewickley bituminous) gives higher concentrations of organic sulfur in proportion to the sulfur content of the coal when due consideration is given to the steam to coal ratios employed. Wyoming (Rock Springs) coal - a younger bituminous coal - also gives a higher concentration of organic sulfur in the gas in proportion to the sulfur content of the coal, again giving due consideration to the steam:coal ratio used.

It is important to note from the foregoing that the organic sulfur concentration in the gas is not necessarily proportional to the sulfur content of the coal. It is especially important to observe the decreased concentration of organic sulfur in the gas when the steam:coal ratio is increased. The data on Sewickley bituminous coal illustrate this.

The experiment in which hydrated lime was added to the coal feed to the small gasifier (table 2) was carried out primarily to investigate the possibility of lowering the slagging temperature of the ash, since it is planned to operate the Bureau's pressure gasifier with the ash slagging. A laboratory experiment had shown that a ratio of 0.35 pound of lime per pound of ash (0.038 lb. lime per pound of coal) gave the greatest lowering of the ash

fusion temperature. Use of this lime:coal ratio in the gasifier had no effect on the hydrogen sulfide content but did apparently lower the organic sulfur content of the gas. Doubling this lime:coal ratio resulted in much lower hydrogen sulfide and organic sulfur concentrations in the gas. In passing, it may be noted that this would not ordinarily be an economical method of gas purification; addition of lime to the coal feed would be of interest only where it is desired to operate a slagging gas generator with a coal of high ash-fusion temperature.

It is planned to carry out further studies of the relation between sulfur content of the coal and organic sulfur concentration in the gas under various operating conditions. Experiments with Kentucky coal containing probably 5 percent sulfur are planned, among others.

DETERMINATION OF ORGANIC SULFUR

With the exception of the determination of thiophene, no attempt has been made in the Morgantown laboratory to develop methods for determining individual organic sulfur compounds. Several methods, presented in the literature, for identifying and determining individual types of sulfur compounds were tried, but results were quite erratic, particularly with low concentrations. A report on the Morgantown method for determining thiophene in synthesis gas, based on the isatin reaction, is in preparation.

Most of the analytical work was directed toward improving or developing methods for determining total organic sulfur. In catalytic removal processes where the sulfur content of the purified gas must not exceed 0.1 grain of sulfur per 100 cu. ft., the need for a quick and accurate method of analysis is evident.

The methods which were investigated included: (1) Combustion methods, with the resulting sulfate determined turbidimetrically, colorimetrically, and titrimetrically, and methane dealing with the organic sulfur compounds; and (2) conversion to hydrogen sulfide, with the sulfide determined colorimetrically.

Combustion Methods

Combustion methods, although time-consuming, were studied because of their value as primary standards for comparison in evaluating more convenient methods, such as those depending on the catalytic conversion of the organic sulfur compounds to hydrogen sulfide. Even after a catalytic method is once proved, the combustion method is of value for rechecking where there is a possibility that interfering substances are present or where unusual gas-making conditions might conceivably yield unusual organic sulfur compounds not amenable to catalytic conversion.

Referees' Method

This classical method for determination of total sulfur in gas has been in use for over 100 years and requires no detailed description here.

This method and some of its modifications are described by Altieri.^{7/} To use this method, with gravimetric determination of barium sulfate, requires 50 hours if the gas is burned at a rate of 0.5 cu. ft. per hour and the sulfur content is as low as 0.1 grain per 100 cu. ft. This would give only 0.0127 gram of barium sulfate; any appreciable contamination of the barium sulfate could result in a proportionally large error. Other objections to the standard Referees' method are the lack of provision for using purified air for combustion, need for replenishment of the ammonium carbonate, possible incomplete scrubbing of the combustion gases (especially if the gas rate is increased), use of cork or rubber stoppers, and use of a wet test meter which may absorb or give up sulfur compounds.

Because of the widespread acceptance of the method or modification thereof by State regulatory bodies and the manufactured-gas industry, it was considered desirable to investigate the possibility of modifying the method to eliminate some of the objectionable features. Moreover, the method of absorbing the sulfur dioxide in the ammoniacal condensate from the combustion products appeared to have merit since it eliminates the use of gas washing bottles used in other methods. Gas washing bottles - especially the more efficient types with fritted disks - give considerable back pressure and generally require a suction pump to exhaust the products of combustion.

Briefly stated, modifications made in the Referees' apparatus were to provide for purification of the combustion air, supply of ammonia vapor by passing the air for combustion through a large bottle of ammonium carbonate, and replacement of cork or rubber stoppers by the use of interchangeable ground-glass joints. All of the holes in the standard Referees' burner assembly - except one - were sealed. Through the remaining hole, air that had been purified by passage through sulfuric acid, alkaline potassium ferricyanide, and activated carbon was introduced. The ammonium carbonate was placed on the stream between the purifying train and the burner.

The bead column of the original apparatus was replaced with a Friedrich's condenser. This permitted increased rates of combustion since better cooling was effected. A glass flowmeter was used instead of a wet test meter. It was found possible to burn gas at a rate of 1.4 cu. ft. per hour, and it is believed this could probably be increased.

To make possible more accurate determinations with very small amounts of barium sulfate, a turbidimetric method employing the Betz-Hellige turbidimeter was used. This method - also employed in other combustion methods - will be discussed in a later section of this report.

Table 4 gives results obtained from the Bureau's modified Referees' method as compared with the I.G.T. burner method. The standard gas used was a mixture of carbon monoxide and hydrogen from a cylinder.

^{7/} Altieri, V. J., Gas Analysis and Testing of Gaseous Materials: Am. Gas Assoc., Inc., New York, 1945, pp. 148-150.

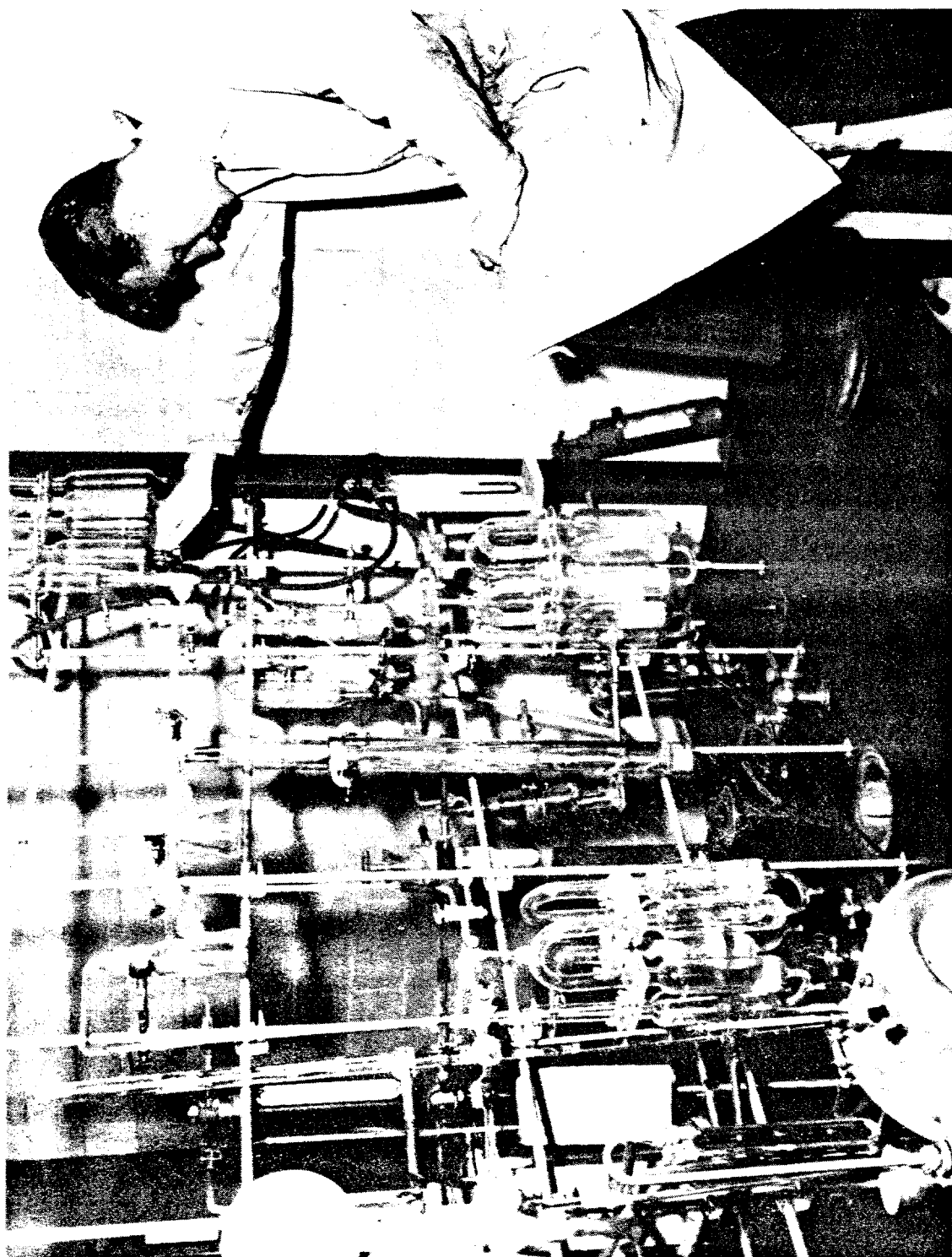


Figure 1. - I. G. T. apparatus for the determination of organic sulfur in gas.