

CHAPTER 5. - GAS PURIFICATION

Contents

	<u>Page</u>
Status of gas purification in 1944.....	78
Bureau of Mines contributions to gas purification, 1944-55.....	79
Research.....	80
Impurities in synthesis gas.....	80
Analytical methods for dust determination.....	80
Particle size.....	81
Analytical methods for sulfur compounds.....	81
Sulfur poisoning of methanation catalyst.....	84
Process development.....	84
Studies of dust-removal processes.....	84
Dust removal in atmospheric-pressure pilot plant.....	84
Dust removal in high-pressure pilot plant.....	85
Sulfur- and CO ₂ -removal processes.....	87
Activated carbon.....	87
Hot carbonate scrubbing.....	90
Gas purification in the demonstration plants.....	94
Technology yet to be solved.....	94
Dust removal.....	94
Sulfur and CO ₂ removal.....	96
Literature cited.....	97

Illustrations

<u>Fig.</u>		
27.	Uniform dry dispersion of dust showing concentration near edge of dish.....	82
28.	Uniform dry dispersion of dust for determining particle-size distribution, shown at higher magnification.....	83
29.	Effect of carbonyl sulfide poisoning on activity of a nickel catalyst used for methanation.....	85
30.	Performance of high-pressure dust scrubber.....	86
31.	View of gas-purification pilot plant.....	88
32.	Correlation of carbon dioxide:hydrogen sulfide ratios in raw gas with composition of acid gas from reactivation of foul phosphate scrubbing solution.....	89
33.	Effect of carbon dioxide:hydrogen sulfide ratios in raw gas on composition of acid gas obtained in reactivation of potassium N-dimethyl glycine absorbent.....	90
34.	Agitator absorber tested for use in gas purification.....	91
35.	Pilot plant for removing carbon dioxide from synthesis gas by hot carbonate scrubbing.....	92
36.	Schematic diagram of pilot plant for hot carbonate scrubbing.....	93
37.	Equipment for removing sulfur from synthesis gas in Bureau of Mines demonstration plant.....	95
38.	Scrubber for laboratory tests on removal of dust from gas.....	96

TablePage

7. Cost of removing 1,000 cu. ft. of carbon dioxide from synthesis gas at 300 p.s.i. absorber pressure.....	94
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Raw synthesis gas from coal contains both dust and gaseous impurities, and these impurities must be removed before the gas can be used for the synthesis of liquid fuels. Certain impurities, such as the sulfur compounds in the gas, are particularly deleterious in the Fischer-Tropsch synthesis, where they poison the catalyst. This problem has been studied at several Bureau of Mines establishments.

Status of Gas Purification in 1944

The bulk of investigative work on purification of synthesis gas for producing synthetic liquid fuels had been carried out in Germany. Reports of the Combined Intelligence Objectives Sub-Committee and of the British Intelligence Objectives Sub-Committee following World War II included data on the purification of synthesis gas to the degree required for its conversion to liquid fuels (11). Except for the Lurgi pressure-gasification process, the various gas-producing processes operated substantially at atmospheric pressure and were followed by purification processes operating at approximately the same pressure.

European practice (16) for purifying raw synthesis gas, whether produced from coke or directly from coal, normally utilized combinations of the following processes:

1. Selective removal of hydrogen sulfide, using potassium N-dimethyl glycine (Alkazid DIK), or simultaneous removal of hydrogen sulfide and carbon dioxide, using potassium N-methylalanin (Alkazid M).
2. Removal of residual hydrogen sulfide with iron oxide purifiers.
3. Removal of gum-forming compounds and thiophene with activated carbon.
4. Removal of the remaining organic sulfur compounds by catalytic conversion and simultaneous absorption, using alkalized iron (approximately 70 percent iron oxide and 30 percent sodium carbonate).

Other gas-purification processes were available but found only limited use. Among these were processes for removing hydrogen sulfide and carbon dioxide with alkali hydroxides and sodium or potassium carbonate solutions and the old process of oxidizing hydrogen sulfide to elemental sulfur over activated carbon. Because of the high heat release, this latter process was used only with gases containing relatively low concentrations of hydrogen sulfide.

Sulfur-recovery processes were in widespread use throughout Europe. The most widely used was that of Claus, in which hydrogen sulfide was oxidized to elemental sulfur (14). Another process for recovering sulfur, which was developed in Europe and still finds only limited application in this country, was extraction of sulfur from spent iron oxide, generally with carbon disulfide or ammonium polysulfide.

Except in purification of gas for ammonia synthesis, purification processes in this country in 1944 were generally operated at low pressures. Numerous processes were commercially available for removing hydrogen sulfide, such as the iron oxide, Seaboard, vacuum carbonate, Thylox, and Girbotol. The organic sulfur content of ammonia synthesis gas (whose purity specifications are in many ways similar to those for the Fischer-Tropsch synthesis) was reduced by scrubbing with caustic soda. Other gases, such as natural gas and coke-oven gas, did not require as stringent purification as does synthesis gas for the manufacture of liquid fuels. Purification of synthesis gas for producing high-B.t.u. gas was not of immediate interest in 1944, although a few companies were concerned about our future supply of natural gas.

Raw synthesis gas as obtained from coke in water-gas sets is relatively dust free, and any dust present is removed in the conventional condensing and scrubbing operation. On the other hand, synthesis gas produced directly from pulverized coal is highly contaminated with dust, so dust removal becomes an important part of the general synthetic fuels problem.

Although dust removal had been relatively unimportant in the production of water gas, a variety of dust-removing equipment had been developed for use with other types of industrial gases. Large cyclones and knockout chambers were used for rough removal; small cyclones, scrubbers, etc., for further purification; and electrostatic precipitators, Theisen disintegrators, or filters of various types for reducing the dust concentration to extremely low values. The moving-bed filter was used in a few places in Germany for fine purification.

Bureau of Mines Contributions to Gas Purification, 1944-55

The Bureau of Mines gas-purification research and development program, started in 1946 at Morgantown, had two main objectives:

1. Developing processes operable at pressures up to 450 p.s.i.g., for reducing the total sulfur content of raw synthesis gas to less than 0.1 grain per 100 std. c.f.^{8/} and the carbon dioxide content to less than 4 percent by volume, and for removing dust. Pressure purification reduces space requirements by increasing throughput and usually results in more efficient operation.

2. Research toward recovery of sulfur. Important credits might result from sale of byproduct sulfur; also, venting of any large quantity of sulfur to the atmosphere would be undesirable.

^{8/} Throughout this chapter, volumes of gas were calculated, according to a gas industry standard, as dry gas at 60° F. and 30 in. Hg.

Accurate and rapid analytical procedures were required to evaluate various purification processes and to determine whether purified synthesis gas met specifications, so the work included development of suitable analytical methods.

Research

Impurities in Synthesis Gas

Total sulfur in the gas produced at Morgantown increased linearly with the sulfur contents of the various coals gasified. These coals contained from about 0.5 to 5 percent sulfur. In general, regardless of the rank of coal, hydrogen sulfide concentration in the gas ranged from 160 to 190 grains per 100 std.cu.ft. and organic sulfur from 6.5 to 9 grains for each percent of sulfur in the coal gasified (22). All organic sulfur was present as carbonyl sulfide. Of the sulfur in the coal fed to the gasifier, about 70 to 80 percent appeared in the product gas stream, about 20 percent in the residue, and about 8 percent in the scrubber water.

The amount of carbon dioxide in the raw gas depended to a considerable extent on the steam:carbon ratio used in the gasification step; for example, in the Morgantown atmospheric-pressure gasifier the product gas contained about 10 percent carbon dioxide with a steam:carbon ratio of 0.5 pound per pound and 22 percent carbon dioxide with a ratio of 1.6. The oxygen:carbon ratio and residence time have some effect on carbon dioxide formation but considerably less than the steam:carbon ratio.

Analytical Methods for Dust Determination

The weight of dust in the gas was determined by the conventional use of Soxhlet extraction thimbles as filters. This method proved satisfactory under most conditions, and hundreds of dust determinations were made by it at various points in the several gasification systems. The thimbles were unsatisfactory, however, for testing hot crude synthesis gas coming from the top of the gasifier, because the high concentration of dust filled the thimbles in a short time and the high concentration of moisture wet the thimbles unless they were kept heated to a temperature above the dewpoint of the gas. A satisfactory method that was developed involved collecting and condensing most of the dust and moisture in flasks and then removing the remaining dust with a large filter paper and the remaining moisture with a drying agent. This method has the advantage of including determination of the concentration of moisture as well as of dust (10).

The conventional thimble method also was unsatisfactory for testing highly purified gases, because extremely long sampling times were required to accumulate enough dust to weigh accurately. An improved drying procedure was developed for decreasing weighing errors when thimbles were used for dust determinations (10). Later a large-area filter holder was devised to decrease the sampling time (10). These methods were used to determine dust and moisture concentrations over a wide range of conditions, with concentrations of dust varying from thousands of grains to less than 0.01 grain per 100 cu. ft.

In order to protect the synthesis catalyst, compressors, and other equipment, a synthetic liquid fuels plant using pulverized coal will require a sensitive instrument that will determine the concentration of dust in the gas continuously at critical points in the system and give immediate warning whenever the concentration becomes too high. A photoelectric smoke meter, specially modified by the manufacturer, still did not have enough sensitivity for extremely pure gases (18). However, commercial apparatus of suitable sensitivity later became available, through development in air-pollution work.

Particle Size. - The size of particles over 43 microns is determined most readily by analytical screens. For smaller particles many methods are used, such as elutriation, sedimentation, and permeability to airflow. Although more difficult and tedious, a better method for initial research work is the actual measurement of particle size under a microscope. A method was devised for obtaining uniform dispersion of particles, so that size distribution could be calculated from a count over part of the area (10). Such a dispersion is shown in figure 27, and in higher magnification in figure 28. Particles were concentrated near the edge but were distributed uniformly elsewhere.

Particle-size distribution, as determined by these dispersion methods, can be used as a criterion of the performance of dust-removing equipment only if particles do not exist as agglomerates in the gas stream. This can occur from static electrification, moisture, or other conditions, or from the adhesive properties of the particles themselves. For determining the true agglomerate size in the gas stream, a plastic filter with very fine openings, called a membrane filter, was found highly satisfactory. Particles and agglomerates remained where they hit the smooth filter, so that agglomerates could be viewed and measured with the microscope. Black particles were readily determined, but small white particles could not be seen on white filters. Blue filters were found satisfactory for both black and white particles.

Analytical Methods for Sulfur Compounds

Significant advances were made in developing sensitive analytical techniques applicable to gases in which only traces of impurities could be tolerated. For determining the total organic sulfur content of either raw or purified synthesis gas, the modified platinum spiral method was developed and adopted because of its speed and accuracy (15). This method employs a hot platinum spiral as a catalyst and utilizes the hydrogen in the gas to reduce all the organic sulfur compounds commonly found in gas from partial combustion of coal (that is, carbonyl sulfide, carbon disulfide, thiophene, and ethyl mercaptan) to hydrogen sulfide. The resulting hydrogen sulfide is then determined colorimetrically by the methylene blue method (13).

No attempt was made to develop methods for determining individual organic sulfur compounds other than thiophene and carbonyl sulfide. The colorimetric method for determining thiophene sulfur is based on the reaction between thiophene and isatin, resulting in the characteristic deep-blue indophenine color. A procedure was developed and proved valid. As little as 0.0001 grain of thiophene sulfur per 54.5 ml. of test solution can be detected (23).



FIGURE 27. - Uniform Dry Dispersion of Dust Showing Concentration Near Edge of Dish (top of picture).

FIGU

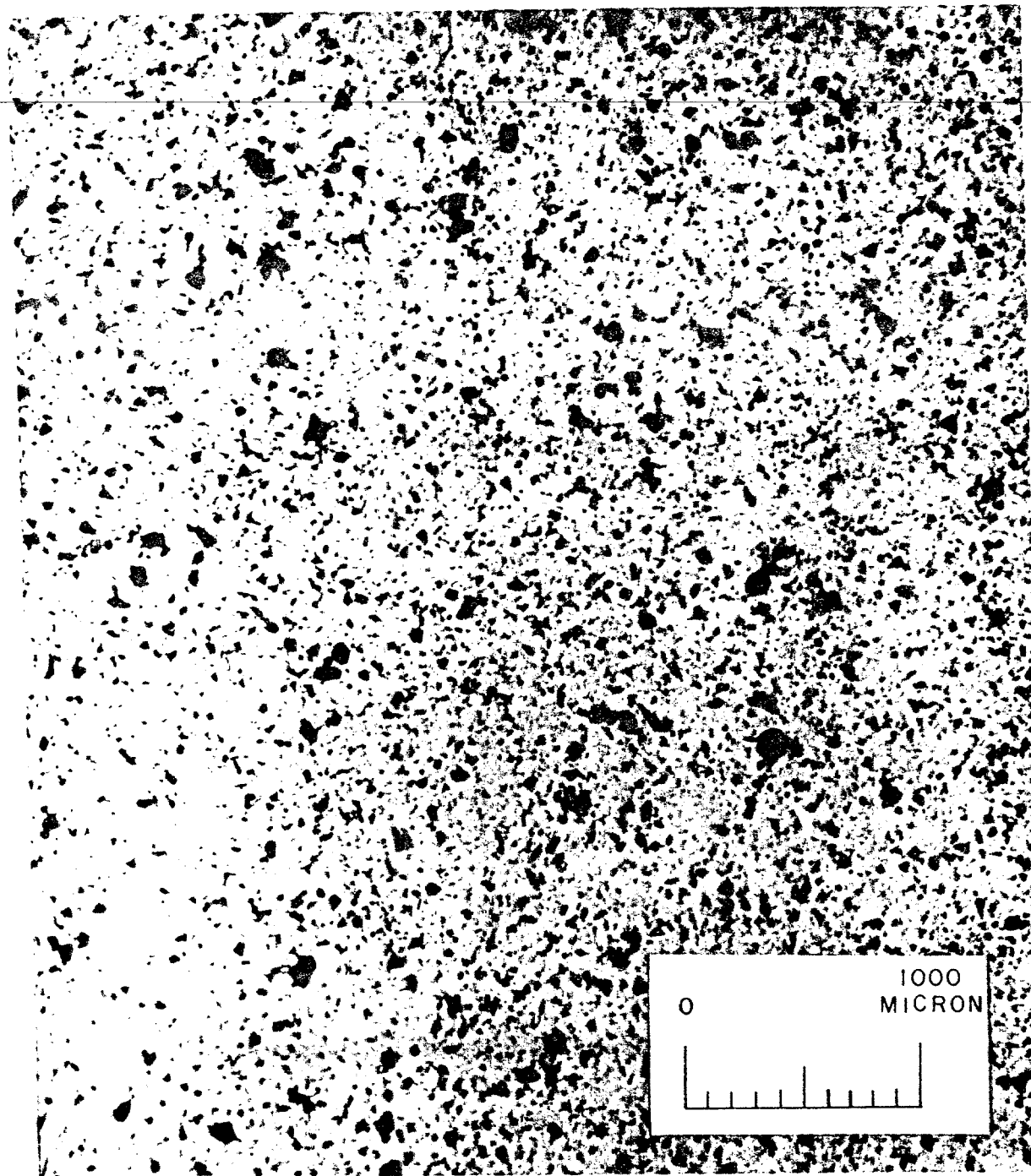


FIGURE 28. - Uniform Dry Dispersion of Dust for Determining Particle-Size Distribution, Shown at Higher Magnification.