Electron-Microscope Studies of Coal and of Fischer-Tropsch Catalysts

The high resolving power of the electron microscope was used to determine the size distributions and surface areas of very finely crushed coal particles.[5] The results of this study should be of value in the improvement of processes utilizing pulverized coal, such as combustion in boiler furnaces, turbines or diesel engines and hydrogenation to form synthetic gasoline and oil. Large numbers of particles were measured on micrographs of several coals and petrologic constituents. The weight percentages of particles in regular size groups were calculated from the cube of the linear dimension measured, and the resulting distributions were plotted on special graph paper of the type shown in figure 1. This paper was devised on the basis of the Rosin-Rammler law of size distribution, which has been shown to apply to coal particles large enough to be measured by sieving. The law can be stated by the equation $R = 100e^{-\left(\frac{x}{\bar{x}}\right)^n}$ where R is the weight percent of sizes larger than x, and x and n are constants. If logarithms are taken twice, then $\log \log \frac{100}{R} = n \log x - n \log \bar{x} + \log \log e$. This is the equation of a straight line when $\log \log \frac{100}{R}$ is plotted against $\log x$. The scales in figure 1 are proportional to those functions of R and x. The suitability of this distribution equation can then be judged by the nearness of the experimental points to straight lines. The constant n in this equation, called the distribution constant, is equal to the slope of the line, and the scales are so related that this is directly the tangent of the angle of the line with the axis of the abscissa. The absolute size constant, $\bar{x}$, is equal to the size at which the line crosses the 36.79-percent ordinate. The value of $\bar{x}$ for a coal sample shows the general range of sizes and n varies with uniformity of sizes. Small values of $\bar{x}$ and large values of n, such as are found in this study, indicate fine particles that are not much different in size. With increasing size, $\bar{x}$ increases and n decreases. Figure 1 shows distribution data for a low-volatile bituminous coal from the Pocahontas No. 3 bed, West Virginia, for a high-volatile A bituminous coal from the No. 5 Block bed, West Virginia, and for petrologic constituents of the latter coal. In addition, data from a study by Perrott and Kinney[6] with the optical microscope of a sample of minus 200-mesh anthracite culm are plotted to show the application of the law to larger subsieve sizes. The agreement of the points for each sample with straight lines leaves little doubt that the Rosin-Rammler law applies quite closely to those fine sizes of coal.

An equation for calculating the surface area of fine coal samples was derived from the Rosin-Rammler law. The exact expression contains an infinite expansion, but very good approximations can be obtained from the

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5/ McCartney, J. T., Determination of the Size Distribution of Fine Coal Particles by the Electron Microscope: Bureau of Mines Rept. of Investigations 3827, 1945, 11 pp.

6/ Perrott, G. St. J., and Kinney, S. P., The Meaning and Microscopic Measurement of Average Particle Size: Jour. Am. Ceram. Soc., vol. 6, 1923, pp. 417-439.

following simplified form, $S=\frac{6}{\rho x}\Gamma\left(1-\frac{1}{n}\right)$ where S is the area per gram, K and n are the Rosin-Rammler constants, ρ is the density, and Γ (the Greek gamma) is the symbol for a gamma function that can be found in statistical tables. The areas of the coal samples discussed were calculated by this equation, and the results are given in table 3. To show the suitability of this equation, the areas were also calculated from the average particle diameter, d, using the equation $S=\frac{6}{\rho d}$. An appropriate shape factor was applied to the measured particle dimension (x) to obtain a value of d suitable for use in this form of equation for area. Columns 5 and 6 of table 3 show the areas obtained by the two methods. This investigation shows that the complete size distribution and surface area of a sample of powdered coal can be obtained by using simple sedimentation or elutriation methods to determine the weight percent of particles above or below two or three sizes. The Rosin-Rammler line may be drawn from these data.

Fine coal particles, when subjected to high pressures, show tendencies toward plastic deformation. It appears that differences in the effects of these forces applied to particles of various ranks of coal are of such small magnitude that the high resolving power of the electron microscope is required to reveal the phenomena clearly. The method of applying the high pressure, with simultaneous observation of the sequence of effects, involves placing very fine particles of coal under a cover glass on a microscope slide, observing these under an optical microscope, and applying pressure on the flexible cover glass with a strong needle. Intermittent application of pressure attained by moving the needle back and forth or with a rotary motion is required. The coal particles under pressure are seen to flatten and spread. With some types of coal, a plastic flow ensues, which continues until the particle becomes a thin translucent film. Other coals, however, seem to disintegrate into much finer particles, and it is those that can best be studied in the electron microscope. This technique was applied to particles of vitrain and fusain selected from various ranks of bituminous and anthracite coal. Figure 2 shows electron micrographs illustrating the effect of high pressure on vitrain particles from a number of coals. Some evidence of plastic flow can be seen in all of these, but the greatest deformation occurs in the high-rank bituminous and in the semianthracitic coals. Coals of lower rank behave in the same general way but do not become as fluid. The anthracitic and meta-anthracitic coals tend to disintegrate into extremely fine particles. Fusain particles from a few coals showed similar differences, although the variations do not correlate regularly with rank of coal. Fusain from one subbituminous coal became fairly fluid, while that from another subbituminous coal behaved like vitrain from meta-anthracite, and fusain from a low-volatile bituminous coal reacted like an anthracitic vitrain. The significance of these differences in the effects of pressure has not yet been thoroughly analyzed. However, it appears that there are variations in the petrologic constituents, not readily discernible by usual optical means, that the electron microscope can help to reveal. Such differences may help to explain anomalies recently encountered in attempts to correlate petrologic character with degree of plasticity induced by heat in the coking process.

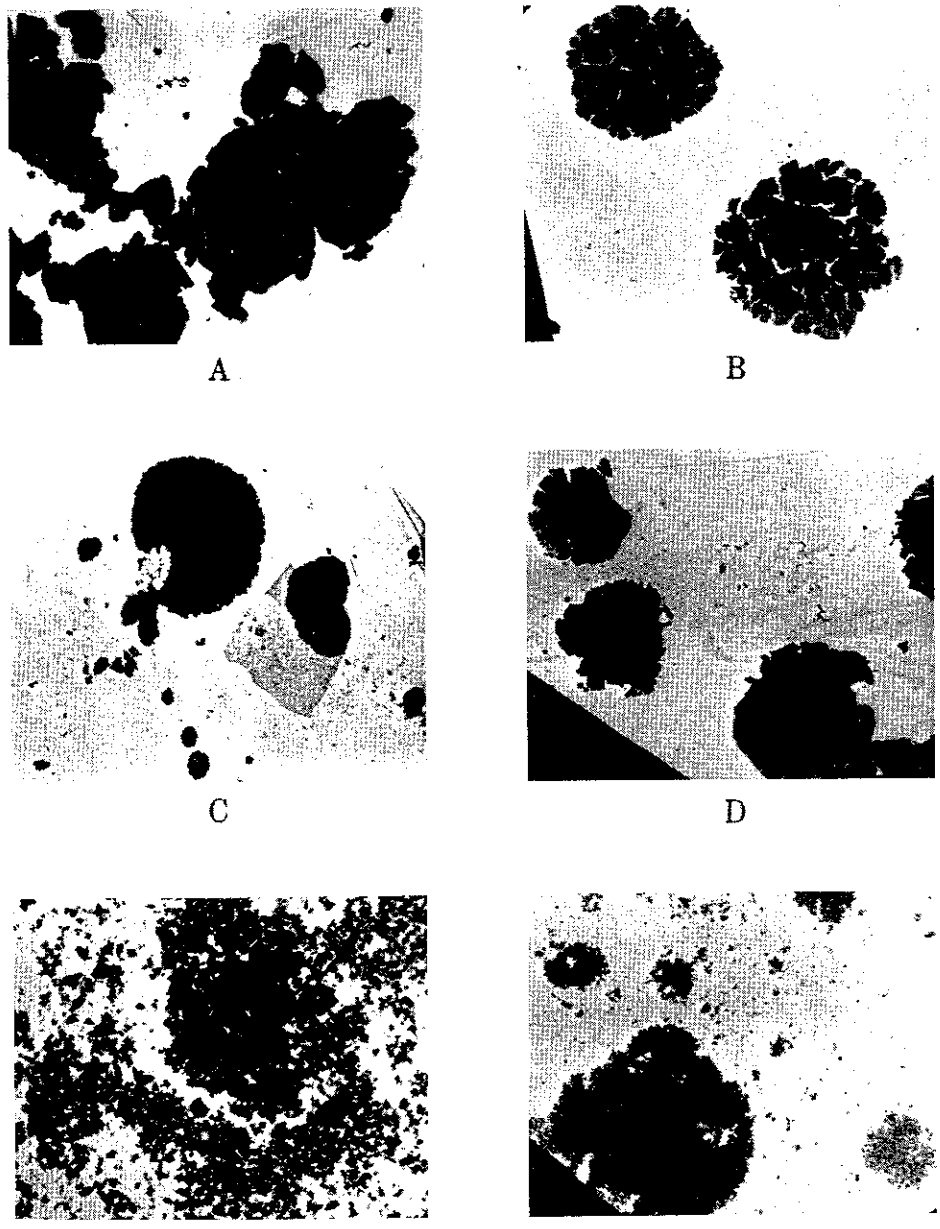

Figure 2. - Electron micrographs of compressed particles of vitrain from coals of various ranks: A, Subbituminous; B, high-volatile bituminous; C, low-volatile bituminous; D, semianthracite; E, anthracite; F, meta-anthracite. 2100X.

TABLE 3. - Surface areas of fine coal samples determined by the electron microscope

Coal sample	Density, gm. per cc. ρ	Absolute size constant, microns $\bar{x}$	Distribution constant n	Surface area, sq. m. per gm., calculated from	
				Ave. diam.	Rosin-Rammler law
Vitrain from No. 5 Block bed coal....	1.3 (est.)	.50	2.13	30.9	36.5
Fusain from No. 5 Block bed coal.....	1.4 (est.)	.82	2.41	17.5	18.6
Pocahontas No. 3 bed coal.....	1.3	.84	2.58	17.3	18.8
Durain from No. 5 Block bed coal.....	1.6 (est.)	1.66	2.25	7.9	8.6
No. 5 Block bed coal.....	1.4	2.11	1.95	8.1	8.7
Anthracite culm (optical microscope).	1.8	38.8	1.45	.36	.58

A catalyst used in the Fischer-Tropsch synthetic liquid-fuel process, consisting of cobalt oxide as the active unreduced catalyst, thorium oxide and magnesium oxide as promotors, and kieselguhr as a carrier, was studied by the electron microscope. Cobalt oxide and several types of kieselguhr were also studied. Figure 3 is a micrograph of the mixed catalyst. The large diatom with the regular pattern of round holes is characteristic of kieselguhr. Its effectiveness as a carrier is probably the result of this open structure, which permits the reacting gases to penetrate freely to the active ingredients. The particles and aggregates seen on the micrograph range in size from several microns down to 0.01 micron. Calculations from the effective surface area of this catalyst measured by a nitrogen-absorption method indicate that, if the material were composed of nonporous particles, their average diameter would be 0.015 micron or about the size of the smallest particle shown on the micrograph. Apparently the larger particles are either aggregates of these very small ones or are porous enough so that gases can readily penetrate them. Since calculations of surface area from electron micrographs depend on the visually apparent particle size, such measurements obviously would not show the area effective in catalyzing the Fischer-Tropsch synthesis. Measurements made on a number of micrographs of the cobalt oxide gave an area of 4 square meters per gram compared to 62 square meters per gram obtained by the nitrogen-absorption method.

Tests of Miscellaneous Materials

In addition to the 248 samples of coal that were tested in connection with the survey of their coking properties, 235 samples of miscellaneous materials, submitted by various sections of the Bureau of Mines or by others authorized to have analyses made, were analyzed and reported during the year. The samples represented a wide variety of materials from many sources. Thirteen boiler-water compounds and 30 boiler scales, sludges, or deposits were analyzed in connection with work on boiler feed-water conditioning to increase efficiency of boilers operated by the Government. Analyses of 47 external deposits from boiler and superheater tubes were made in connection with an investigation of the formation of external corrosive deposits. Phosphine was determined in acetylene produced from 18 samples of calcium carbide as a part of an investigation of the cause of explosions of acetylene generators in western shipyards. Chemical analyses were made of 14 coal or coke ashes, and phosphorous was determined in 15 samples of coal and coke. Sulfate was determined in 17 samples of alcohol and water solutions used in an investigation of a method of estimating surface moisture in crushed coal. At the request of the War Production Board, total iron was determined in the ash of 12 monthly composite samples of coke used in a Defense Plant Corporation blast furnace at Cleveland, Ohio. Determinations of silicon and iron in 8 samples of petroleum coke submitted by the War Department showed that the cokes would meet specifications for making carbon electrodes for the aluminum industry. The remaining 61 samples included rock-dusting materials, mine waters, soot removers, fly ash from furnaces, spent oil shale, residues from compressors in the coal hydrogenation plant, and catalysts used in the Fischer-Tropsch synthesis.

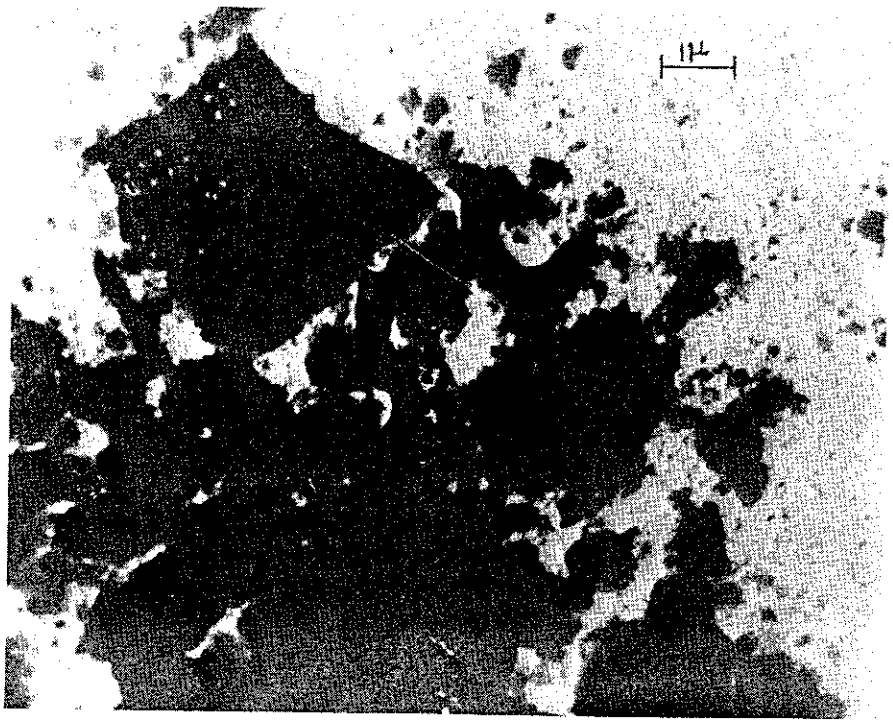

Figure 3. - Electron micrograph of cobalt oxide - magnesium oxide - thorium oxide - kieselguhr catalyst for Fischer-Tropsch synthetic liquid-fuel process. 11,300X.

Determination of Surface Moisture in Coal

Standard methods for determining total moisture in coal are time-consuming, and a knowledge of this moisture content is less useful than the surface-moisture content for control purposes in the coal and coke industry. Total moisture content of wet coal is considered to consist of two components, surface moisture and internal moisture. Presumably, the term "internal moisture" is synonymous with the inherent or bed moisture of coal saturated with moisture but containing no surface water. Surface moisture rather than either total or bed-moisture content controls primarily such physical properties of crushed coal as bulk density and angle of repose. In such processes as drying or dewatering coal in washeries, the real measure of accomplishment is the reduction in surface-moisture content.

To meet the need for a rapid, accurate method for determining surface moisture in coals, an experimental study was made which showed that surface moisture in high-rank eastern bituminous coals can be determined with satisfactory accuracy for most control problems by absorbing this moisture in a concentrated alcohol solution.1/ The method is based upon the change in specific gravity of alcohol caused by the absorption of water. Surface water dissolves quickly in alcohol, whereas the internal moisture is essentially unaffected. Usually 500 to 600 grams of coal, accurately weighed, and exactly 500 milliliters of alcohol are used in contact with each other for exactly 3 minutes. Specific gravity readings estimated to the fourth decimal place and temperature to the nearest 0.1° C. of the alcohol are determined experimentally before and after each test. The temperature correction for specific gravity is 0.0008 per °C. deviation from the base in the range ordinarily used in the tests. Percentages of alcohol by weight before and after the test are taken from a graph prepared from results of known mixtures of water and of the particular alcohol used, or, if the alcohol is of known purity, prepared from accepted data in published literature. The water absorbed by the alcohol is calculated as follows:

$$\text{Water from coal, grams} = V_i d_i \, (A_i/A_f - 1),$$

where V_i is the initial volume of alcohol, in milliliters; d_i is the initial density of the alcohol, in grams per milliliter, A_i is the initial percentage by weight of alcohol; and A_f is the final percentage by weight of alcohol.

The particle size of coal is not important as long as excessive amounts of very fine coal are not present. The alcohol can be used until it contains about 50 percent of water; the lowest limit has not been determined. Testing technique was developed so that the surface-moisture determination can be completed in less than 15 minutes. Alcohols, such as ethyl and isopropyl, are better than methyl for differentiating between surface moisture and internal moisture.

Correlations of the data obtained for surface moisture by this method on coals as crushed for coke-oven charges with data for total moisture on the same coals as determined by the A. S. T. M. standard method, which uses a drying oven at 105° C. and a coal sample passing a U. S. Standard No. 60

1/ Schmidt, L. D., and Seymour, W., A Rapid Method for Determining Surface Moisture in Coal: Bureau of Mines Rept. of Investigations 3811, 1945, 11 pp.

sieve, gave straight-line relationships. The total moisture in samples of the same coal, but of different moisture contents, can be closely approximated by addition of a constant to the determined surface moisture. This constant can be determined once for all for a given coal from the straight-line relationship found between surface moisture and total moisture. Preliminary studies of lower-rank bituminous and subbituminous coals have shown less constancy between the surface and total moisture contents, as determined by the two methods. In such coals the alcohol extracts some of the internal or bed moisture and gives high results for surface moisture. Research studies are being continued to enable a finer distinction to be drawn between surface and internal moisture, to improve the technique and precision on eastern coals, and to extend application of the method to lower-rank coals.

Analyses of Ash from Coals of the United States

Ash composition is a fundamental property of coal which determines its clinkering and slagging characteristics when burned on grates or in the form of powdered coal. Composition of ash is also important in the selection of coal for special purposes, such as cement manufacture and the burning of the finer grades of ceramic products. A compilation[8] of over 200 analyses of coal ash, including many ash-fusibility temperatures was made from Bureau of Mines laboratory records to show the ash composition of various coals of the United States. The report includes a discussion of the nature and occurrence of ash-forming mineral matter in coal and the relationships between ash composition and ash fusibility. Common mineral constituents determined in routine coal-ash analyses are given. Coal ash from coals of the United States varies widely in chemical composition but generally comes within typical percentage limits as follows: Silica, 20 to 60; aluminum oxide, 10 to 35; ferric oxide, 5 to 35; calcium oxide, 1 to 20; magnesium oxide, 0.3 to 4; titanium oxide, 0.5 to 2.5; sodium and potassium oxides, 1 to 4; and sulfur trioxide, 0.1 to 12.

Calorific Value of Coal

The calorific value of coal was discussed with reference to definitions, laboratory methods for its determination, formulas for calculating calorific value from coal analyses, the constancy of calorific value of coal in limited geographical areas, and its use as a basis for coal classification.[9]

Physical Properties of Coal

The hardness, strength, friability, and grindability of coal and methods of estimating these properties were reviewed, and the relationships of grindability of coal to rank and pulverizer performance were discussed.[10]

8/ Selvig, W. A., and Gibson, F. H., Analyses of Ash from Coals of the United States: Bureau of Mines Tech. Paper 679, 1945, 20 pp.

9/ Selvig, W. A., and Gibson, F. H., Calorific Value of Coal: Nat. Research Council (H. H. Lowry, ed.), Chemistry of Coal Utilization, New York, vol. 1, 1945, pp. 132-144.

10/ Yancey, H. F., and Geer, M. R., Hardness, Strength, and Grindability of Coal: Nat. Research Council (H. H. Lowry, ed.), Chemistry of Coal Utilization, New York, vol. 1, 1945, pp. 145-159.