CARBONIZATION AND ITS PRODUCTS

Thermal Decomposition of Coal

Knowledge of the mechanism and kinetics of tar formation and its conversion at higher temperatures to high-temperature tar is important in the carbonization industry. The mechanism of tar formation appears to be intimately associated with the mechanism of coke formation, development of coke strength, and expansion characteristics of the coal; thus, knowledge of tar formation and its reactions will lead to better understanding of the coking mechanism.

As one means of studying the mechanism of coke and tar formation, the Bureau is studying the composition and yields of gases, liquids, and residues formed by carbonizing small samples of coal under various pressures at 300° to 550° C. At constant carbonizing temperature the total volume of gas decreased as the absolute pressure above the coal decreased.

In a related study a bed of coal fluidized by steam or nitrogen has been used, and provision was made for recovering the overhead products directly, as in conventional carbonization practice or after passing them through a cracking unit at 600° to 800° C. (fig. 8). Superficial velocities of the fluidizing mediums of 3.5 to 3.9 feet per second are best for tar production when a mixture of 14- by 35-mesh high-splint coal and char is fed. Char yields from the fluidized carbonizer are much lower than those obtained in the BM-AGA apparatus; but tar yields are much greater, and the tar contains much more pitch. Fluidization with steam or nitrogen produced essentially the same yields of acids, bases, aromatics, olefins, and paraffins. Except for approximately equal yields of olefins, yields of these products from fluidized carbonization are less than those from BM-AGA carbonization. A preliminary study in a thermal cracker shows that, when the cracking temperature is increased from 600° to 700° to 800° C., the yield both of the liquid portion of the tar (boiling below 350° C.) and of the pitch decreases progressively. This same behavior is observed in BM-AGA carbonization.

Expansion During Carbonization

Expansion test data are of particular interest to coke-oven operators because of the danger of oven damage from coals or blends that expand excessively during coking. As part of the survey of carbonizing properties of American coals, expansion tests in the sole-heated oven are made only on those coals that contain over 65 percent dry, mineral-matter-free fixed carbon.[52] Experience has shown that most coals of lower rank contract during carbonization. ~~During 1957, 14 coals from Pennsylvania and West Virginia were tested.~~ Although the sole-heated oven requires a charge of 18 kilograms of coal for a test, a much smaller-scale test with only 71 grams gives results that correlate well with the larger scale test and may well be useful in carbonization studies, particularly where the amount of sample is small.

---

[52] Naugle, B. W., Wilson, J. E., and Smith, F. W., Expansion of Coal in the Sole-Heated Oven: Quantitative Effects of Dry Bulk Density, Moisture Content, and Particle Size: Bureau of Mines Rept. of Investigations 5295, 1957, 15 pp.

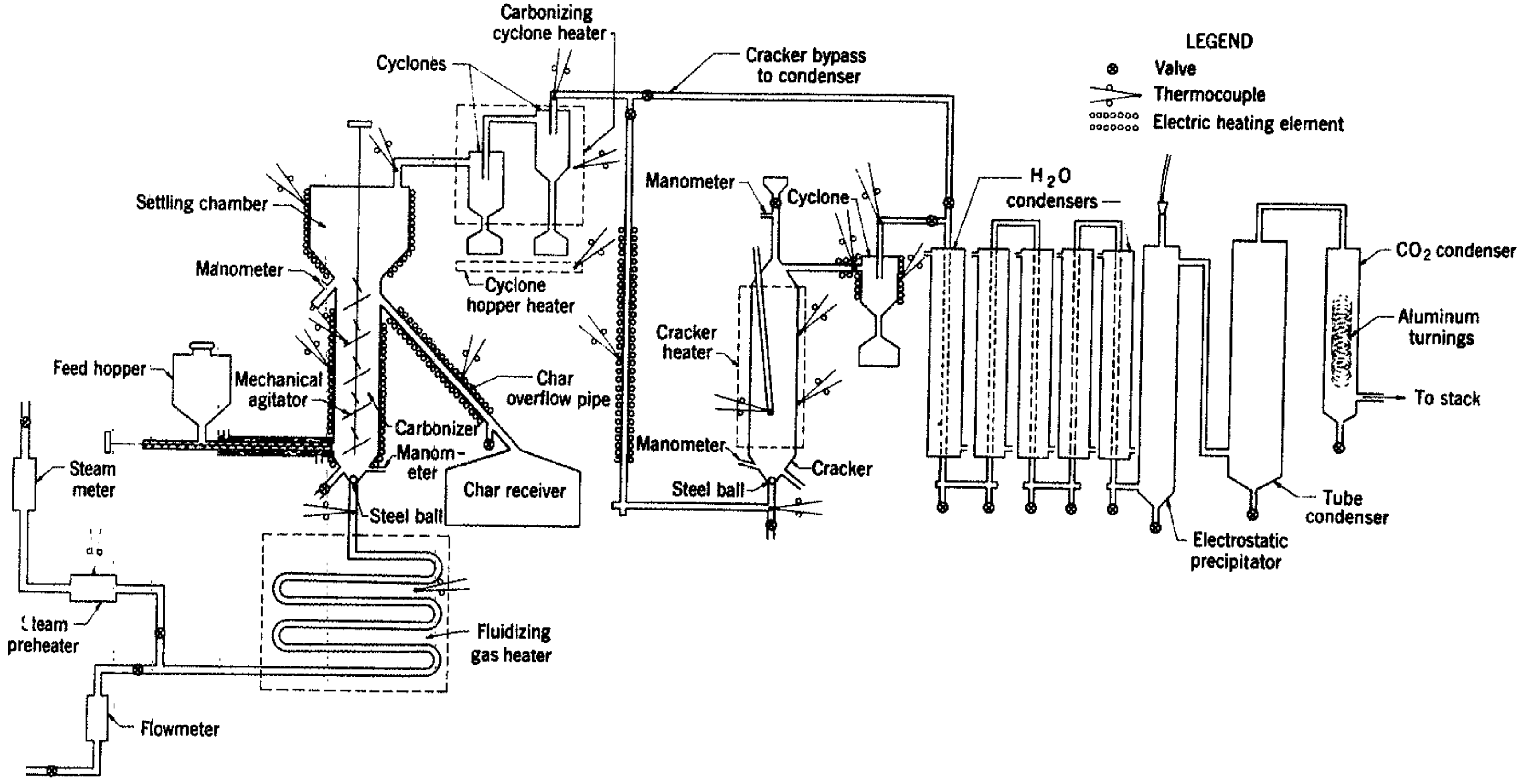

FIGURE 8. - Equipment for Studying Mechanism of Coal Carbonization.

Effect of Pretreatment on Carbonization

Pretreatment of low-rank coals, particularly at temperatures below their softening points, improves the quality of the cokes obtained from their subsequent carbonization. This finding has special significance concerning production of improved metallurgical coke from western coals.

A high-volatile western coal, pretreated in an inert atmosphere at 215° C. and subsequently charged hot to a test oven, yielded a coke with a tumbler stability index twice that of coke obtained from direct carbonization. Pretreatment was less effective when the hot charge was allowed to cool before final carbonization. In another study a blend of Hiawatha coal from Carbon County, Utah, with 15 and 25 percent of a medium-volatile mixture of three coals from the Wilkeson area, Wash., yielded a stronger coke when preheated to 320° C. in steam than with no pretreatment, the tumbler stability indexes being 37 compared with 28, and the tumbler hardness indexes being 63 compared with 59.

Effect of Cleaning on Carbonization

A program on the effect of cleaning on coal carbonization was initiated in 1957. The mineral matter from which coal ash is formed may be considered a naturally occurring inert material in coal that affects the structure of coke, as do other inerts that are sometimes intentionally added to coal before carbonization. The petrographic composition of coal and hence the structure of its coke may also be altered by cleaning. Thus, removal of fine coal almost certainly results in removal of most of the fusain, small amounts of which result in a blockier coke.

Stockton-Lewiston coal from Kanawha County, W. Va., was cleaned at 1.45 specific gravity. The following samples were carbonized in the BM-AGA 18-inch retort at 900° C.: (1) Unwashed coal, (2) float fraction of the washed coal, and (3) float-and-sink coal recombined in proportions equivalent to the unwashed coal. The principal effect of cleaning was a reduction in ash content from 18.7 to 9.2 percent. The sulfur content of the unwashed coal was low (0.6 percent), and cleaning had no effect on it. Washed coal yielded coke with a lower 1-1/2-inch shatter index but higher tumbler indexes. This effect accords with previous data, which had shown that the addition of inerts increases the shatter index but decreases the tumbler indexes. The recombined sample of cleaned coal and refuse showed the same carbonizing properties as the original coal.

Effect of Fluidity on Abradability of Coke

The fluidity of a coal, as measured by the Gieseler plastometer or a similar instrument, is commonly believed to be a decisive factor in determining the strength of coke made from it. Fluidity may be changed by additions of inert material in fine sizes, such as high-temperature coke, silicon carbide, or activated carbon; the strength of the char prepared from the mixture is measured by a modified Roga abrasion test.

Two coals, one from the Lower Freeport bed of Clearfield County, Pa., having a maximum Gieseler fluidity of 15,000 dial divisions per minute, and the other from the Upper Freeport bed of Cambria County, Pa., having a maximum Gieseler fluidity of only 44 dial divisions per minute, were blended with varying proportions of an inert. Much larger proportions of inert were necessary to reduce to a minimum the strength (abrasion index) of the char obtained by carbonization of the coal-coke blends containing the more fluid coal. The strength of the char increased rapidly in the fluidity range of zero to five dial divisions per minute. Beyond this range the char strength was virtually independent of the fluidity. The difference in the char strength for the two coals of different levels of maximum fluidity was small when the fluidities of the respective blends were five dial divisions per minute.

The specific character of the inert material greatly affected the strength of char made from binary blends with coal. Silicon carbide appeared to narrow the plastic range of a coal much less than activated carbon when increasing amounts were added to progressively decrease the plastic range of this coal. Greater porosity and adsorptive capacity of the activated carbon limit the amount of cementing material available for binding the particles together. The abrasion indexes of chars obtained from blends containing small proportions of either silicon carbide or activated carbon and large proportions of coal were slightly higher than that of char from the unblended coal.

Coking Properties of Western Coals

In the cooperative program on improving the quality of coke made from western coals 21 high-temperature carbonization tests were run in the 500-pound, 14-inch, slot-type coke oven. Auxiliary studies were also made in the 50-pound, 10-inch modified BM-AGA retort, the 100-gram carbonization test, and the Parry-Potter dilatometer. Results and discussion of the complete series of 30 slot-oven tests and all auxiliary studies have been reported to the cooperating organizations. In general, the results show that the average size of coke decreased when the carbonization temperature was increased. The plus-1.06-inch tumbler index decreased slightly when the carbonization temperature was increased. Increased carbonization time in the experimental slot oven was shown to be proportional to the increased bulk density. Coke produced at low bulk densities generally had better physical properties than corresponding cokes produced at higher bulk densities.

Carbonizing Properties of Bituminous Coals

The objective of the continuing survey of carbonizing properties of American coals, in the BM-AGA apparatus to determine yields and properties of coke and other products at a carbonizing temperature of 900° C., is to evaluate the carbonizing properties of the principal coalbeds of the United States.[53] This evaluation will provide the metallurgical industry with information about the suitability of coals for making metallurgical coke. During 1957, 22 coals from West Virginia and 4 from Pennsylvania were tested.

---

[53] Smith, F. W., Reynolds, D. A., and Wolfson, D. E., Coking Properties of Pittsburgh District Coals: Trans. AIME, Min. Eng., vol. 9, No. 3, pp. 360-364.

Boone County, W. Va.

Eleven coals, representing the Stockton-Lewiston, Coalburg, Hernshaw, Chilton, Cedar Grove, and Alma seams, ranked as high-volatile A bituminous. The ash content of nine of the coals ranged from 3.3 to 7.8 percent. One sample of Stockton-Lewiston coal contained 12.0 percent ash, and a sample of Alma coal contained 10.0 percent ash. These coals yielded rather abradable coke, which would probably be improved by cleaning to reduce the ash. Other samples of coal that were obtained from these beds, but contained less ash, yielded a less abradable coke. The two samples of Alma coal were high in sulfur, containing 2.6 and 2.7 percent; this factor would detract from their usefulness as a source of metallurgical coals under present standards. The other coals from this county would be satisfactory as a major constituent of coking blends.

Nicholas County, W. Va.

Five coals, representing the Lower Kittanning, Middle Kittanning, Eagle, and Sewell seams, were low in ash and sulfur content, which ranged from 3.2 to 6.8 and 0.7 to 0.8 percent, respectively. All the coals except the Sewell, which was lowest stratigraphically, ranked as high-volatile A bituminous. Sewell coal ranked low in the medium-volatile classification. The coals yielded coke having satisfactory physical properties for metallurgical coke with tumbler-stability indexes ranging from 38 to 57 and tumbler hardness from 61 to 66.

Logan County, W. Va.

Coals from the Alma and Eagle beds were high-volatile A in rank and had satisfactory chemical properties for metallurgical coals. Their coke properties indicated that these coals would be satisfactory major constituents of coking blends.

Monongalia County, W. Va.

Three coals, one from the Pittsburgh bed and two from the Sewickley bed, ranked as high-volatile A bituminous. Although the physical properties of the coke were satisfactory for coals of their rank, the moderately high sulfur content (2.4 percent) of the Sewickley coals would limit their use as major constituents of coking blends.

Fayette County, W. Va.

Lower Eagle coal, which ranked high in the high-volatile A classification, and Fire Creek coal, which ranked as low-volatile bituminous, had satisfactory chemical properties for metallurgical coals and yielded strong coke. However, coals of these ranks tend to expand excessively when carbonized singly; this factor would limit their metallurgical use.

Raleigh County, W. Va.

A report has been published on the carbonizing properties of Raleigh County coals.[54] Seventeen coals from 13 beds were carbonized singly. To determine the effect of blending the higher rank coals from this county with lower rank coals, five coals were blended with various high-volatile A coals. Raleigh County coals rank as high-volatile A, medium-volatile, or low-volatile bituminous, and this diversity of rank is reflected in the wide variation of the carbonization properties. The higher rank coals yielded the stronger cokes. The blending properties of the low-volatile coals were similar, and the coals can be substituted for each other without significant loss in coke strength of the blends. The expansion of low-volatile coals is not an important factor in blends containing high proportions of high-volatile coal. Although the expanding properties of high-volatile A coals are not closely related to coal rank, the expansion of their blends with low-volatile coal can be estimated from the expansion of the high-volatile component.

Jefferson and Clearfield Counties, Pa.

Three samples of Lower Freeport coal from these counties were high-volatile A and yielded satisfactory coke for coal of that rank. However, the sulfur content of these coals ranged from 2.5 to 3.5 percent; this factor would limit their use as metallurgical coals.

Green County, Pa.

Pittsburgh coal was moderately high in sulfur but could be blended with higher rank low-sulfur coals to yield a satisfactory metallurgical coke.

Indiana County, Pa.

A report has been published on the carbonizing properties of Indiana County coals.[55] Coals in this county rank either high in the high-volatile A or low in the medium-volatile coal classification. Although Indiana County coals produce coke of satsifactory strength for metallurgical use, the variability of their chemical and expanding properties must be considered in their use by the coking industry. The coals contained moderate proportions of ash, but 8 of the 16 coals tested contained over 1.7 percent sulfur, and the maximum was 4.1 percent. The expansion of the coal, as determined in the sole-heated oven, ranged from 19.3-percent contraction to 21.8-percent expansion, therefore, all coals in this county should be tested for expansion before industrial carbonization.

---

[54] Wolfson, D. E., Birge, G. W., and Naugle, B. W., Carbonizing Properties of Raleigh County, W. Va., Coals: Bureau of Mines Rept. of Investigations 5359, 1957, 19 pp.

[55] Wolfson, D. E., Birge, G. W., and Naugle, B. W., Carbonizing Properties of Indiana County, Pa., Coals: Bureau of Mines Rept. of Investigations 5314, 1957, 18 pp.

Westmoreland County, Pa.

A report has been published on the carbonizing properties of Westmoreland County coals.[56] One sample from the Redstone, two from the Pittsburgh, and two from the Upper Freeport beds were carbonized in this investigation. Although Westmoreland County coals yield coke with satisfactory physical properties, their use by the coking industry depends on their chemical properties. Four of the coals contained more than 2 percent sulfur. Upper Freeport coals obtained at most locations in the county can be upgraded to meet chemical standards for metallurgical coals, but upgrading of high-sulfur Pittsburgh and Redstone coals would be difficult.

Metallurgical Use of Anthracite

Blends With Bituminous Coal

In recent years economic factors have provided considerable incentive for establishing new markets for anthracite, one possible outlet being in metallurgy, where moderate quantities of anthrafines might be used in coking blends. Studies of the effects of varying the composition of the coal fraction of a blend containing a fixed quantity of anthrafines have been completed.[57] This cooperative work consisted of carbonizing tests in the Tuscaloosa oven of blends in which a number of different high- and low-volatile coals were substituted for those normally used in company coking operations. Comparison of the physical properties of the various cokes indicated several blends that would be expected to yield cokes having physical properties very similar to those produced from the reference blend.

Calcination

Besides being used in blends with bituminous coals, anthracite may be used for blast-furnace and cupola operation, with or without thermal stabilization by calcination.[58] Preliminary foundry tests conducted with anthracite calcined in a vertical-shaft retort resulted in more satisfactory cupola operation than had been obtained with raw anthracite. One-hundred-percent calcined anthracite used as cupola fuel met the foundry requirements for melting rates, temperatures, and fuel-iron ratios. To make further studies of the conditions required to produce maximum quantities of thermally stabilized large-size anthracite and to produce sufficient quantities of fuel for additional foundry tests, a pilot-scale, vertical-shaft calciner having a capacity of 10 to about 500 pounds per hour was constructed (fig. 9).

---

[56] Birge, G. W., and Wolfson, D. E., Carbonizing Properties of Westmoreland County, Pa., Coals: Bureau of Mines Rept. of Investigations 5374, 1957, 12 pp.

[57] Gayle, J. B., Eddy, W. H., and Shotts, R. Q., Effects of Substituting Various High- and Low-Volatile Coals in Foundry-Coke Blends Carbonized in the Tuscaloosa and Sole-Heated Ovens: Bureau of Mines, Rept. of Investigations 5307, 1957, 16 pp.

[58] Eckerd, J. W., Buehl, R. C., and Tenney, R. F., The Suitability of Anthracite for Blast-Furnace and Cupola Operation: Pennsylvania State Univ., Min. Ind. Exper. Sta. Bull. 70, June 1957, pp. 17-28.

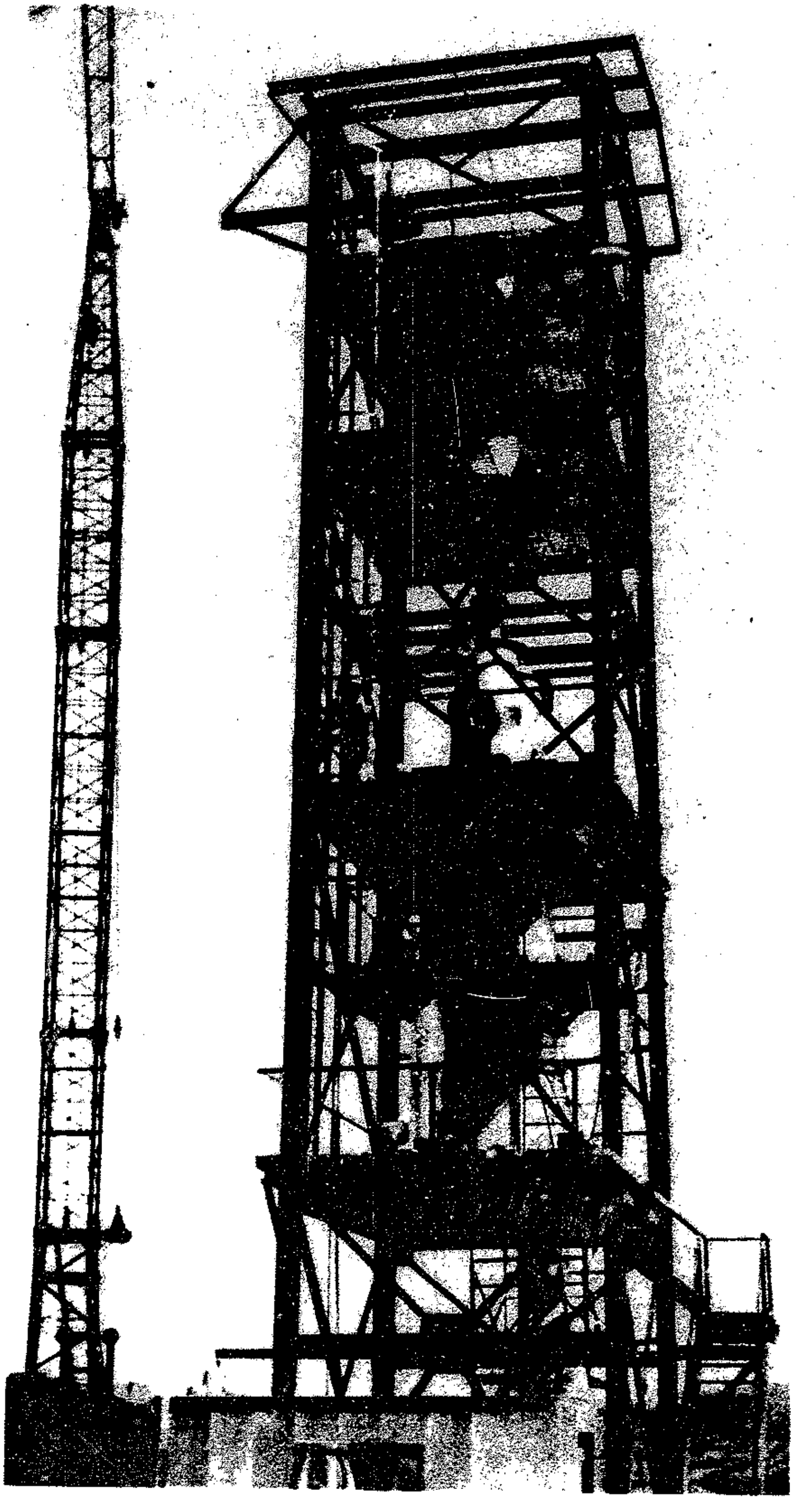

FIGURE 9. - Vertical-Shaft Pilot Plant for Calcining Anthracite.

The calcining characteristics of two types of anthracite have been reasonably well established in this equipment. The first of these, a relatively high-volatile and friable anthracite from the western end of the Western Middle field, has proved to be rather difficult to calcine because it decrepitates to a considerable extent when subjected to either high calcining temperatures (above 1,800° F.) or high throughput rates. When the retort temperature reduced to 1,600° F. and the throughput decreased to about 40 pounds per hour, the yield of plus-1-5/8-inch product increased to 57 percent, but it appeared to be quite friable. In tests with a more stable anthracite from the Northern field throughput rates of approximately 60 pounds per hour were obtained with a yield of 65 to 80 percent of plus-1-5/8-inch product. The product from both anthracites contained approximately 1 percent volatile matter.

To maintain satisfactory operating pressures, the amount of fuel smaller than Stove size (2-7/16-inch by 1-5/8-inch round-hole screens) must be maintained at a minimum in a foundry cupola. In addition, when the ash content of the fuel charge exceeds 12 percent, operating problems are created with regard to both the quality and the amount of slag produced. Satisfactory cupola operation has been achieved only when the fuel contained less than 12 percent ash.

Arrangements have been made to obtain anthracite representing each of the producing areas to study its calcining characteristics. Enough low-ash anthracite will be calcined to make possible further, more extensive foundry tests.

Briquetting

Despite lowering of the thermal decrepitation of anthracite by calcining, its strength as measured by the ASTM Tumbler and Drop Shatter Test for Coke has not been increased materially. To overcome these deficiencies, a laboratory study has been conducted on reconstituting anthracite fines into an agglomerated metallurgical fuel. The work has utilized briquetting, followed by calcination of the preformed product. Coal-tar pitch, asphalt, and sulfite liquor have been evaluated as binders. Two types of bituminous coal were used as mix additives; and effects of size consist, briquetting temperature and pressure, calcination, rate of heating, and final temperatures were evaluated. Briquets formed in a laboratory press at 3,000 p.s.i. and calcined at 1,750° F. were stronger than a good-grade foundry coke. The briquet formulation was 82 percent anthracite, 10 percent bituminous coal, and 8 percent 70° C. m.p. coal-tar pitch. Briquets containing 89 percent anthracite and 11 percent 70° C. m.p. coal-tar pitch were superior in stability factor to metallurgical coke. If this relative strength can be maintained in larger scale production, these blends will be studied as basic metallurgical briquet formulations. A pilot plant is under construction at present to produce large enough quantities of briquets for tests in modern metallurgical equipment and, at the same time, to determine the most satisfactory process conditions. It is expected that the process economics will be at least partly evaluated in the pilot-plant study.

Low-Temperature Carbonization

Wyoming Coals

Production and evaluation of industrial carbons from Wyoming noncoking or slightly caking coals are part of the program concerned with upgrading Western United States coals. Emphasis has been given to the processing of fine and lump coal for the production of char for thermal power, char suitable as a blending material in metallurgical coke manufacture, lump chars that may be substituted for coke breeze in phosphate ore reduction furnaces, and char for manufacturing activated carbons.

Wyoming bituminous and subbituminous coals were processed in bench-scale apparatus to determine potential carbonization yields and in pilot-plant retorts to produce enough char and tar for analysis. These tests have shown that a critical selection of coal is necessary when the coal is processed for a specialized carbon. The type of coal becomes important when carbonization conditions are held constant. Generally, Wyoming bituminous and subbituminous coals produce high yields of tar on carbonization; the yields usually increase as coal rank increases. Characteristically, the low-temperature tars derived from Wyoming coals are high in tar acids. A comprehensive report assessing the carbonizing properties of Wyoming coals is being prepared.

Texas Lignite

A review of recent developments and the status of low-temperature carbonization for generating power was presented before the American Power Conference.[59] The review pointed out that the technical phases of this problem are essentially solved. Economic considerations relating the cost of mining, processing, and yield to the value of solid fuel and tar are complex. These considerations cannot be fully determined until a firm value for low-temperature tar has been established.

Researchers conducted a series of low-temperature carbonization experiments on a dried Texas lignite in the 8-inch-diameter fluid-bed retort, heated both internally and externally, varying the air-lignite ratio. The principal effects of increasing this ratio were a decrease in the yields of char and tar and an increased yield of combustible gas per pound of moisture- and ash-free lignite charged. The decrease of tar is distributed throughout the entire boiling range of the tar, resulting in a significant decrease in tar acids, paraffins, and naphthenes. Gas yields show an increase in all constituents, except hydrogen sulfide, with an increase in transport air. The significant increases, however, may be attributed to carbon monoxide and carbon dioxide. The principal combustible product, accounting for the increase in the gaseous B.t.u. values with increase in transport air, was carbon monoxide. At air-lignite ratios less than 6 standard cubic feet of air per pound of moisture- and ash-free lignite only fixed carbon burned, but at higher ratios portions of both fixed carbon and volatile products burned.

Assay Test

During the past few years interest in low-temperature carbonization of coal has increased, owing to development of new methods, particularly fluidized bed carbonization. The coke or char obtained is a source of smokeless fuel, and the tar is a potential source of raw material for processing into a variety of chemicals. To provide information on the yields of low-temperature carbonization products of American coals, a bulletin was published that gives the results of Fischer-Schrader low-temperature carbonization assays at 500° C. of about 400 coals from nearly every coal-producing State, Alaska, and British Columbia, Canada.[60] The coals ranged in rank from lignite to semianthracite. The report lists the yields of carbonization products, the types of carbonized residue obtained, and the chemical analyses of the coals. The procedure for making the assay is described, as well as a correlation of the yield of carbonization products with the chemical analyses of the coals.

---

[59] Landers, W. S., Low-Temperature Carbonization of Coal and Lignite for Thermal Power Generation: Proc. American Power Conference, Chicago, Ill., vol. 19, 1957, pp. 344-351.

[60] Selvig, W. A., and Ode, W. H., Low-Temperature Carbonization Assays of North American Coals: Bureau of Mines Bull. 571, 1957, 56 pp.

A different, small-scale, carbonization assay test, originally reported in 1953, is now routinely applied to virtually every coal received by the Denver laboratory. The test has passed through a demonstration period of over 8 years on a wide variety of coals and has adequately proved its versatility, both as a standard bench-scale test and as a research tool in carbonization investigations. Its high reproducibility has shown it to be a most useful guide in predicting plant carbonization yields, particularly from coals of lignitic and subbituminous rank. During 1957 more than 60 new samples were studied.

Utilization of Lignite From India

During 1957 rapid advances were made in the program of technical assistance to the Indian Government in connection with utilization of lignite from Neyveli, South Arcot. The background and scope of this program were reported in 1956. Briefly, the major exploitable reserve of mineral fuel now known in southern India is a deposit of low grade lignite near Madras. Earlier Bureau work, released for publication in 1957,61/ had demonstrated the adaptability of the lignite to fluidized drying and to high-pressure, binderless briquetting. Carbonization of such briquets would provide an alternate source of domestic fuel in India, the demand for which is exceeding the available supplies of dried cow dung and charcoal.

Late in 1956 the Bureau contracted with ICA to pursue further research on the problem and to design and procure an integrated pilot plant for installation at the mine site at Neyveli. These objectives were achieved in 1957. The Neyveli pilot plant has several purposes. First, it processes Indian lignite in large enough quantities to provide solid fuel and tar for use studies on the spot. Second, it serves as a proving ground for later industrial units, the detailed design of which will take advantage of lessons learned in the pilot plant. Third, it will be a facility for training Indian technologists in modern techniques of processing lignite and low-rank coal. The plant has been designed with maximum operational flexibility, so that it can be operated with substantial variations in feed material and in drying, briquetting, and carbonizing conditions.

As a part of the long-range plans for lignite utilization in southern India the Bureau also supervised preparation of an engineering study and preliminary design of a plant (figs. 10 and 11). Capacity of the plant was established as 2-1/2 thousand tons of raw lignite per day, although actual mine production is not scheduled to be this large for several more years. (See also under Foreign Activities, p. 25).

Low-Temperature Tar

Three programs are underway for investigating low-temperature tar. One is a study of lignite tar, another of tars from subbituminous and lower rank bituminous coals, and the third of tar from higher rank bituminous coal.

61/ Parry, V. F., Landers, W. S., Wagner, E. O., Goodman, J. B., and Allen, R. R., Utilization of South Arcot, India, Lignite: Bureau of Mines Rept. of Investigations 5351, 1957, 34 pp.

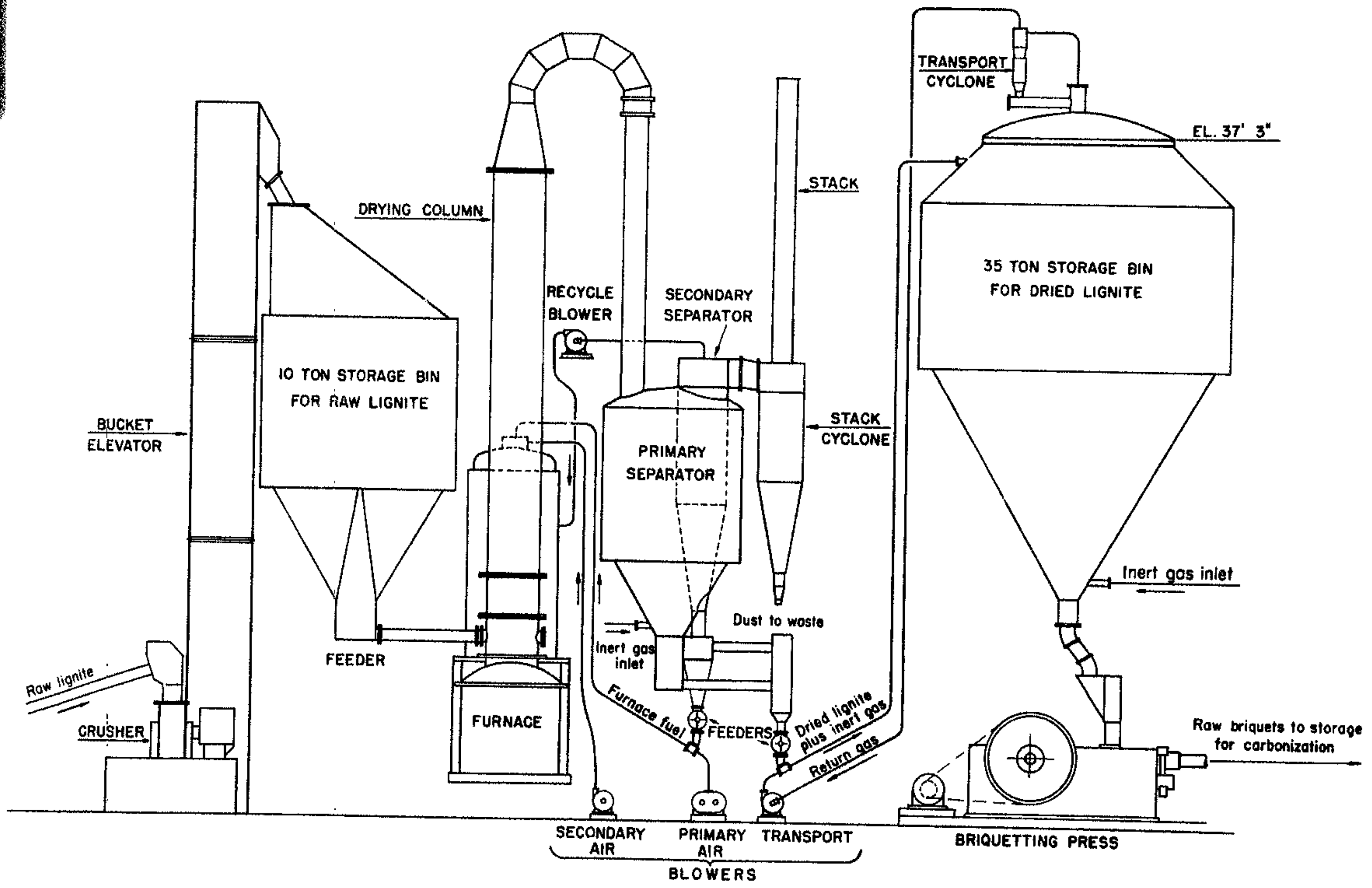

FIGURE 10. - Crushing, Drying, and Briquetting Units for Processing Lignite at Neyveli, India.

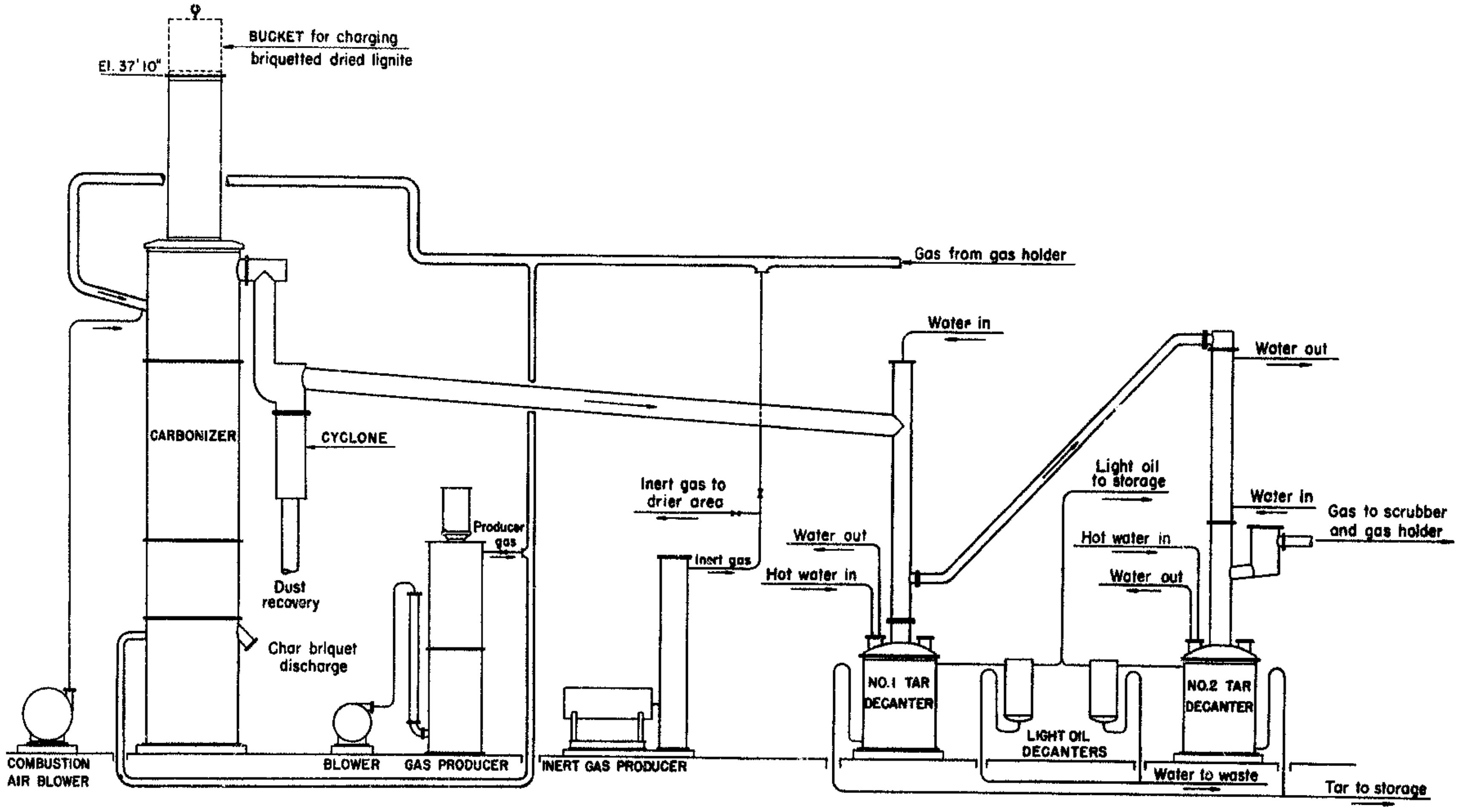

FIGURE 11. - Carbonization and Tar Recovery Units for Processing Lignite at Neyveli, India.

Through this three-pronged attack, it is hoped that the value of low-temperature tar will be increased, aiding economic development of low-temperature carbonization.

Tar From Lignite

The present approach in studying lignite tar is that of detailed characterization of tar fractions by distillation, chemical treatment, chromatography, and examination of absorption spectra. Efforts are being concentrated on the tar acids (phenolics), the more unstable components of the tar.

The most important physical techniques applied to characterization of lignite tar are gas-liquid partition chromatography and infrared absorption spectra. Application of both techniques has been limited essentially to the lower boiling phenolics in the past. The effects of liquid phases and operating conditions on separations of higher phenolics had to be determined. Also, a catalog of reference spectra covering the compounds of particular interest had to be established, necessitating a large amount of laboratory synthesis.

Phenols boiling from 230° to 270° C. have been separated by gas-liquid partition chromatography, but its application to complex mixtures is not yet completely satisfactory; separations of low-boiling phenols present no great problem. The possibility of fractionating tar-acid mixtures by liquid thermal diffusion was investigated, but results have not been satisfactory. A quantitative analysis of the tar acids boiling to 235° C. has been made, and the percentages of 23 individual phenols have been determined.

Tar From Fluid-Bed Carbonizer

One report on the properties of low-temperature tar from a fluidized carbonizer was published during 1957.62/ In later work analyses were made of the tars from fluidized-bed carbonizing tests of 28 foreign and domestic coals varying in rank from lignite to high-volatile B bituminous coal. The 28 coals were from the Western United States, Alaska, Mexico, Ecuador, the Philippine Islands, and India. The samples consisted of six lignites, seven subbituminous C coals, three subbituminous B coals, three subbituminous A coals, two borderline high-volatile C bituminous-subbituminous A coals, two high-volatile C bituminous coals, and five high-volatile B bituminous coals, which show slight agglomerating properties. All coals processed were noncoking and had a heating value of 14,000 B.t.u. per pound (moisture- and ash-free basis) or less. The coals studied had oxygen contents in the range of 11 to 24 percent (moisture- and ash-free basis). Results from the pilot-plant carbonizations indicate that tar acids increase as oxygen increases up to a maximum of 18 percent oxygen; this trend is followed by a decrease in the tar-acid content as the oxygen in the coal increases. If this relationship is confirmed, the total yield of tar acids obtainable from primary low-temperature tar may be correlated with the type of oxygen linkages in the parent coal, rather than with the total

---

62/ Gomez, Manuel, Goodman, J. B., and Parry, V. F., Low-Temperature Tar From Fluidized Carbonizing Reactors: Bureau of Mines Rept. of Investigations 5302, 1957, 44 pp.

oxygen content of the coal. Neutral oil as well as the high-boiling tar fractions increased as total oxygen content of the coal decreased. Both total tar and neutral oil yields increased as heat content in the volatile matter increased.

Carbonization tests conducted on Texas lignite in the 8-inch-diameter fluidized-bed unit indicate that tar yields increased as the char retention time increased, all other conditions remaining constant. The tar acids and neutral oil fractions of the tar distillate and the olefin fraction of the neutral oil also increased with char retention time. Yields of aromatic and paraffin plus naphthene fractions appeared to be independent of char retention time. In another series of tests a Texas lignite was processed in the fluidized unit at 900° to 1,100° F. Small increases in carbonization temperature increased the specific gravity of the resultant tars and decreased the distillate yield and the temperature of tar decomposition.

Tar From Bituminous Coal

Separation and Characterization

At present not much is known about the many types of chemicals of which low-temperature tars are composed. Therefore, the ultimate value of tar separation and characterization lies in the possibility of supplying industry with information about low-temperature tar in enough detail to make its utilization economically and technologically feasible.

The general program for separating low-temperature coal tar was shown schematically in the 1956 report. This program and the general laboratory and instrumental facilities for composition research have been described.63/

During the past year the research on composition of a sample of low-temperature bituminous coal tar progressed far enough so that the first generalities about individual constituents are beginning to emerge. The identities of nearly 100 individual compounds were determined, some on a tentative basis, but most were clearly established. All these compounds fall in the three classes: (1) Tar acids, (2) tar bases, and (3) aromatic hydrocarbons, including benzenes, indanes, indenes, tetralins, naphthalenes, and biphenyls. The tar acids are mostly aromatic in nature, consisting of phenols (including cresols and xylenols), indanols, and naphthols, and the tar bases are also aromatic, consisting of pyridines (including lutidines and collidines), quinolines, and anilines. Because all of these compounds are aromatic, comparisons of molecular structures can be made among the three classes mentioned. In general, the same molecular structures persist through all three classes. The six fundamental aromatic structures are: (1) A benzene-type ring with six carbon atoms; (2) a six-membered aromatic ring with a saturated five-membered ring fused to it; (3) the same structure with one unsaturated, olefinic bond in the five-membered ring; (4) a six-membered aromatic ring with a saturated six-membered ring fused to it; (5) two six-membered aromatic rings fused together to

---

63/ Analytical Chemistry, Laboratory of the Month; Coal Tar Research Challenges Analysts: Vol. 29, No. 1, January 1957, pp. 51A-53A.