

For this study, samples of run-of-oven coke were taken at coke plants in the United States and Canada. Although sampling procedures were directed toward obtaining the highest possible degree of uniformity in the gross samples, it was found necessary to average the test results of a large number of 500-pound samples to reduce normal testing errors to a point where they were not appreciable fractions of the total variations found in a smoothly operating plant. For example, it was deduced that over 100,000 pounds of coke must be screened to determine if ordinary day-to-day variations in screen analysis have appreciable effects on the performance of a blast furnace. Reports on other aspects of testing the physical properties of coke are in preparation.

### Methods of Making Coke

An introductory section was prepared for a chapter on coke in a recently published handbook on fuels and combustion.<sup>68/</sup> Various types of coke and the equipment in which they are made were described. Cokes were classified according to use.

### Low-Temperature Carbonization of Noncoking Coals

Small-scale laboratory low-temperature carbonization assays at 500° C. were completed on 55 samples of coal as part of the survey of properties of western coals. Samples ranging from lignite to high-volatile bituminous B coals were tested, and tar yields ranging from 1 1/2 to 5 1/2 gallons per ton were obtained. It was generally shown that the yield of tar from coal is approximately proportional to the volatile content.

A pilot plant for carbonizing noncoking coal in the entrained and fluidized state was operated successfully on several ranks of coal and lignite. The unit which was used (fig. 12), had a capacity of about 300 pounds of coal feed per hour. The pilot unit combines the new fluidized carbonizer and the fluidized dryer, which has been described in previous publications.<sup>69/</sup> Carbonization is accomplished by passing the dried fine coal upward through an externally heated retort where the coal is fluidized and heated to about 900° F. All products move out the top of the retort. The coal is charged to the retort pneumatically with air, which combines with the char to liberate about half the heat required for carbonization inside of the retort. This method of processing and carbonizing fine material is applicable to all noncoking carbonaceous fuels, as shown by successful operation of the pilot plant on sawdust.

A larger pilot plant using the fluidized-bed drying and carbonizing technique, with a design capacity of 1 ton of coal per hour, was constructed at Denver before July 1, 1951. The same schematic arrangement was applied in the design of a large, commercial-scale pilot plant to treat approximately 25 tons of Texas lignite per hour. Such a unit is of commercial size, and large plants would consist of batteries of these units.

The object of this development work, which was conducted in cooperation with the Texas Power and Light Co., was to find an economical way to process Texas lignite to remove the valuable tars before burning the char for generation of electric power. Results from economic studies completed on large plants for processing 7,000 to 8,000 tons of lignite per day indicate that the char produced for combustion in the power plant will compete with natural gas, costing about 8 cents per thousand cubic feet when there is reasonable return from the sale of the tar.

<sup>68/</sup> Newmser, L. E., *Methods of Making Coke: Fuels and Combustion Handbook* (Allen J. Johnson, editor), McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 130-132.

<sup>69/</sup> Parry, V. F., and Wagner, E. O., *Drying Fine Coal in the Entrained and Fluidized State: Trans. Am. Inst. Min. and Met. Eng.*, vol. 187, 1950, pp. 974-982; *Min. Eng.*, vol. 187, September 1950, pp. 974-982.

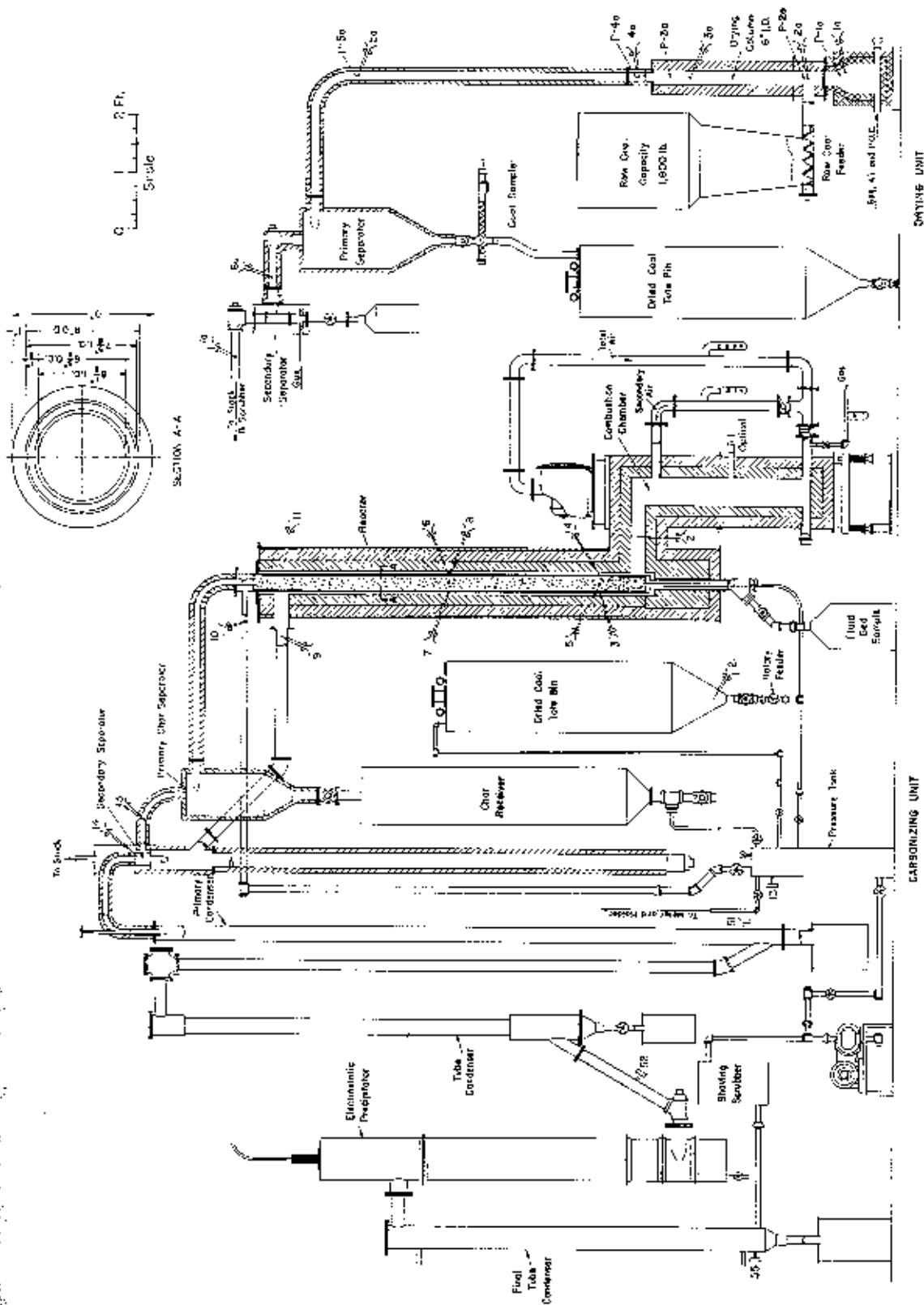


Figure 12. - Pilot plant for fluidized carbonization of noncoking coal; capacity, 250 to 300 pounds per hour.

CARBONIZING UNIT

CARBONIZING UNIT

Low-temperature tars, containing up to 32 percent crude tar acids, are produced from typical Texas lignite by this process. These phenolic compounds and the higher-boiling homologues are potentially valuable in the plastics, wood-preservative, and tar-chemical industries. Gas produced in the process is used for supplying the heat necessary for carbonization. When carbonizing at 900° F., about 10 percent more gas is formed than is necessary for heating. In a large plant the temperature of carbonization would be adjusted to produce just enough gas to carry out the process. Under these conditions the overall thermal efficiency is approximately 88 percent.

Experimental work was conducted during the year on the briquetting of chars which were produced from the process described above to make domestic fuels, to substitute for charcoal. The char is very reactive; when bonded with starch it makes a smokeless briquet that burns almost like charcoal. Studies on the manufacture of substitutes for charcoal in Mexico, Cuba, and other foreign countries indicate that satisfactory fuels can be produced from various low-grade coals.

#### Desulfurization of Coal During Carbonization

A low-ash, good-coking, abnormally high-sulfur (7.5 percent) coal from Ledo Colliery, Assam, India, was effectively desulfurized by carbonization at 800° C. in the presence of added ammonia gas.<sup>10/</sup> The desulfurizing effect was increased still further by addition of aluminum oxide to the coal before carbonization with ammonia, or by addition of sodium carbonate or lime before carbonization with ammonia, and leaching out the soluble sulfur from the cokes.

#### Phenol and Cresols in Coal Tar

Tar samples from BM-AGA carbonization tests at 800° and 900° C. of five American coals were investigated for their contents of phenol and cresols.<sup>11/</sup> Tar-acid mixtures extracted from the dehydrated tars were fractionated and analyzed by the infrared spectrometer. Contents of phenol and each cresol isomer were reported on the dry tar and dry, ash-free coal.

### GASIFICATION OF COAL AND LIGNITE

#### Lurgi Process

An investigation of the Lurgi process<sup>12/</sup> for complete gasification of coals with steam and oxygen under pressure was carried out in three stages. In the first stage, 11 Alabama coals were tested in a 4-inch generator, which proved too small and difficult to control. A 6-inch batch generator, which was provided with facilities for superheating the steam-oxygen mixture and for synthesizing additional methane, was used in the second stage, in which Alabama and West Virginia coals, "Disco," and anthracite were used. In the third stage, a continuous generator of 1-square-foot grate area, similar in design to commercial German generators, was used. Results of the investigation showed that: (1) caking coals could not be used unless their caking power was destroyed; (2) noncaking fuels, such as anthracite and low- and high-temperature cokes, can be completely gasified; (3) although it was possible to gasify samples having a wide range of sizes, the optimum size range of the generator was 1/6- to 3/4-inch; (4) with the proper fuel size, a gas-making capacity as high as 9,000

<sup>10/</sup> Ghosh, J. K., and Brewer, R. E., Desulfurization of Coal During Carbonization, High-Sulfur Indian Coal: Ind. Eng. Chem., vol. 42, 1950, pp. 1550-1558.

<sup>11/</sup> Bengtsson, Erik, (revised by R. E. Brewer), Phenol and Cresols in Coal Tar from Coals Carbonized at 800° and 900° C.: Bureau of Mines Rept. of Investigations 4755, 1950, 10 pp.

<sup>12/</sup> Cooperman, J., Davis, J. D., Seymour W., and Ruckes, W. E., Lurgi Process: Use for Complete Gasification of Coals with Steam and Oxygen under Pressure: Bureau of Mines Bull. 498, 1951, 38 pp.

cubic foot per hour per square foot of gasification area was obtained; (5) the heating value of the carbon dioxide-free gas from bituminous char was about 420 B.t.u. per cubic foot, which dropped slightly at high capacities; (6) using the British nickel methanization catalyst, gas (free of carbon dioxide) of about 950 B.t.u. per cubic foot was synthesized from the Lurgi gas; (7) the soda-iron oxide catalyst used to convert and remove organic sulfur required 10 to 15 times the volume of the nickel catalyst because of its slow action.

### Lignite Gasification

Investigation of the continuous gasification of lignite in the externally heated annular retort at the lignite pilot plant at Grand Forks, N. Dak., was continued during the year. Results of three tests conducted in the pilot plant are given in table 13.

TABLE 13. - Results of gasification tests of lignite, 1951

Test No.	Gasification, hours	Natural lignite used, pounds	Gas made, cu. ft. (S.G.C.) <sup>1/</sup>
14.....	692	370,110	8,228,423
15.....	166	257,908	4,812,512
16.....	637	306,220	6,965,045
Total.....	1,995	934,576	20,058,010

<sup>1/</sup> S. G. C., standard gas condition; saturated gas at 60° F. and 30 inches of mercury.

The alloy retort tube is the heart of the gasification unit. The present 310 alloy tube is the fourth in a series that has been tested and is by far the most satisfactory tube. It has been in operation 3,767 hours, or approximately as long as the other three tubes combined, and has handled more lignite and has produced considerably more gas than the other three tubes. At the end of the year the tube was still in entirely satisfactory condition for further operation, and there was no indication as to its probable minimum useful life.

The gasification of lignite in this pilot plant, the design and operating problems of the plant, and the analyses of the gases produced under various operating conditions have been published.<sup>13/</sup>

A review<sup>14/</sup> was published of the gas-composition data taken in the various test runs and worked out as a basis for correlating the results. The composition of the gases, the H<sub>2</sub>/CO ratio, the heating value of the gas, and the gas production per unit weight of carbon gasified are shown to be related to the fraction of undecomposed steam present in the product gas.

### Underground Gasification

Interest in underground gasification of coal has been widespread. The possible advantages of underground gasification are summarized as follows: A reduction in invested capital costs; the recovery of the energy of the coal in an easily used

<sup>13/</sup> Holtz, J. C., Gasification of Lignite in the Commercial-Scale Pilot Plant at Grand Forks: Proc. of the North Dakota Academy of Science, vol. 4, November 1950, pp. 39-42.

<sup>14/</sup> Chetrick, M. H., Undecomposed Steam in Lignite Gasification: Bureau of Mines Rept. of Investigations 4738, 1950, 11 pp.

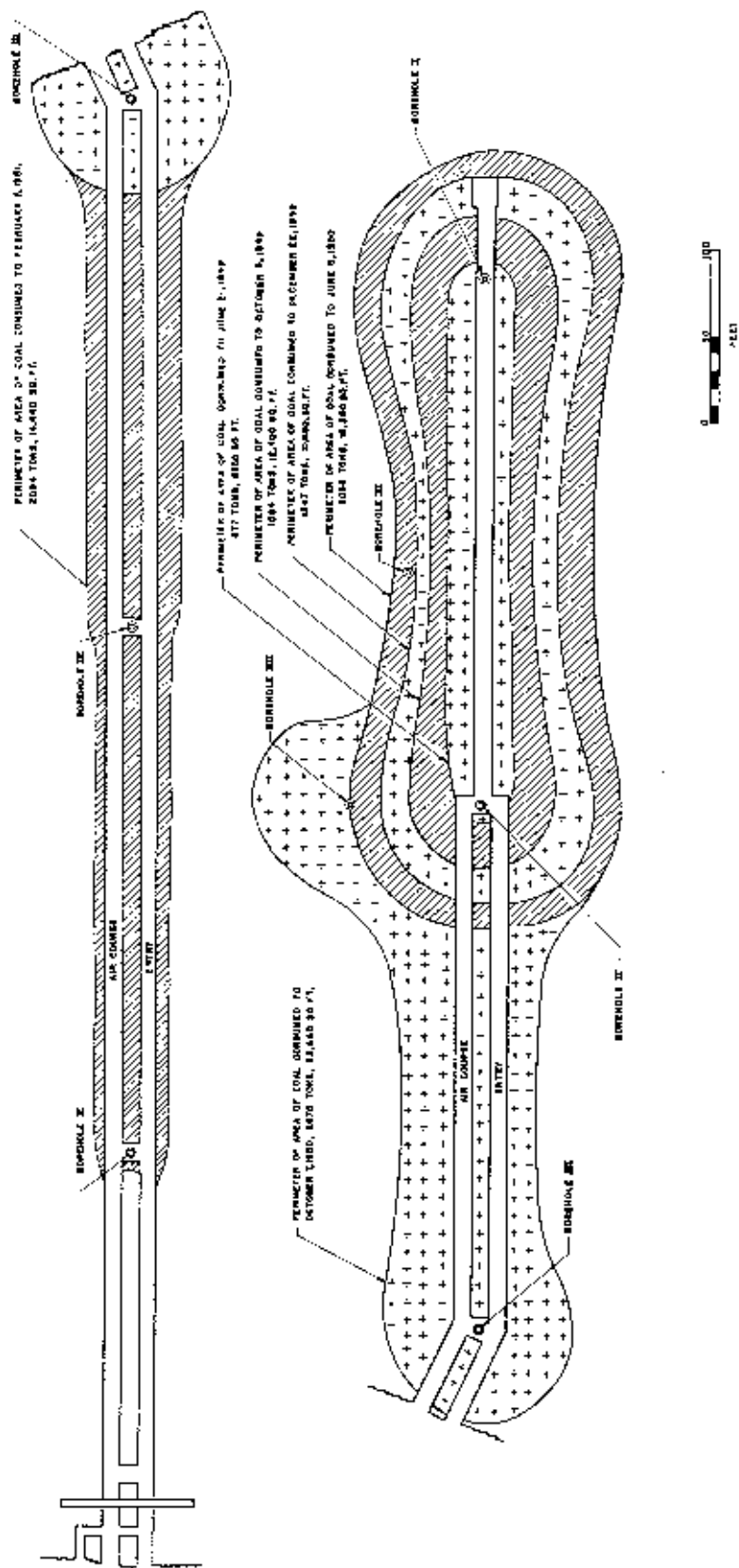


Figure 13. - Coal consumed and area of burned-out region, underground gasification test, Gorgas, Ala.

form; a reduction in over-all labor requirements; the utilization of coal deposits now unminable because of thickness, impurities, or other reasons; and the elimination of the conditions now existing in underground mining that are hazardous to personnel.

The second underground gasification project conducted jointly by the Bureau of Mines and the Alabama Power Co. in the Pratt coal bed at Gorgas, Ala., was continued under fire until February 1951, when operations ceased and flooding of the system with water was started. 75/76/77/78/

Figure 13 shows a horizontal section along the dip of the bed, the upper part of the figure indicating the development work from the outcrop to borehole III and the lower part showing the development from borehole III to borehole I, where the major portion of the coal was consumed in this operation. From March 1949 through May 1950 operation of the experiment was confined to the area of the coal bed between boreholes I and II (fig. 13). During this phase imperfect contact between the injected air and the exposed faces of the coal bed resulted in low calorific values in the effluent gases, and the energy of the coal was brought out of the ground largely as sensible heat. Injection of fluidized sand into the prepared entries and into burned areas of the coal bed resulted in some improvement in operating conditions. The use of long periods of unidirectional air-gas flows (whereby the gas issued at high temperatures, and the combustible constituents of the gas were burned upon contact with unreacted air in or near the outlet borehole) resulted in high effluent gas temperatures and aided in the recovery of the energy of the coal as the sensible heat of the gaseous products.

Following this phase, a large-diameter vertical borehole (VI) was drilled away from the original entry line and intersected the coal bed near the reacting face. When used as an outlet, gas having a calorific value of 90 B.t.u. per cubic foot was produced, but after a few days operation the borehole was rendered useless by the development of excessively high temperatures. Another borehole (VII) was constructed near the reacting face and operated in conjunction with a fresh section of the original prepared entry. Operation of this second unit, including the area between boreholes III and VII, was started in June 1950.

Initially, a lean combustible gas was produced at borehole VII. The air input was limited to avoid damage to the exit borehole. Low-calorific value gas was produced at borehole III. With time, gas equality declined at each outlet; after 4 months a gas having a calorific value of 20 B.t.u. per cubic foot was produced at either outlet under normal operating conditions. Oxygen appeared in the gas a week after starting operation in the section and increased in amount with time.

While operating between boreholes III and VII, two aircraft-type turbocharger units were installed at borehole III to operate by hot gas from the system,

- 15/ Elder, J. L., and Graham, H. G., Experimentation on Underground Gasification of Coal: Mines Mag., vol. XXXI, October 1950, pp. 107-111, 117, 124.
- 16/ Fies, M. E., and Elder, J. L., Experiments on Underground Gasification of Coal Continue at Gorgas: Am. Gas Jour., vol. 173, July 1950, pp. 15-18.
- 17/ Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1951. Part I. Oil from Coal: Bureau of Mines Rept. of Investigations 4770, 1951, 74 pp.
- 18/ Elder, J. L., and Wilkins, E. F., The Underground Gasification of Coal in the U.S.A., an Outline of the Bureau of Mines Experiments at Gorgas, Ala., Jour. Inst. Fuel, vol. XXIV, May 1951, pp. 94-99.

as shown in figure 14. The compressed air from the superchargers was added to that from the reciprocating compressor and injected underground. Early in these tests, the gas ignited underground as a result of the combustible constituents uniting with the free oxygen. Gas-discharge temperatures ranged from 1,000° to 1,400° F. Pressures became stabilized at 18 p.s.i.g. air-inlet pressure and 12 p.s.i.g. gas-outlet pressure. Under these conditions the oxygen content of the gas decreased to zero, and the turbine discharges burned freely. No unreacted air reached the outlet borehole. The operation of the turbines qualitatively demonstrates a means of recovering the sensible heat of the gases while simultaneously creating more favorable conditions for gasification.

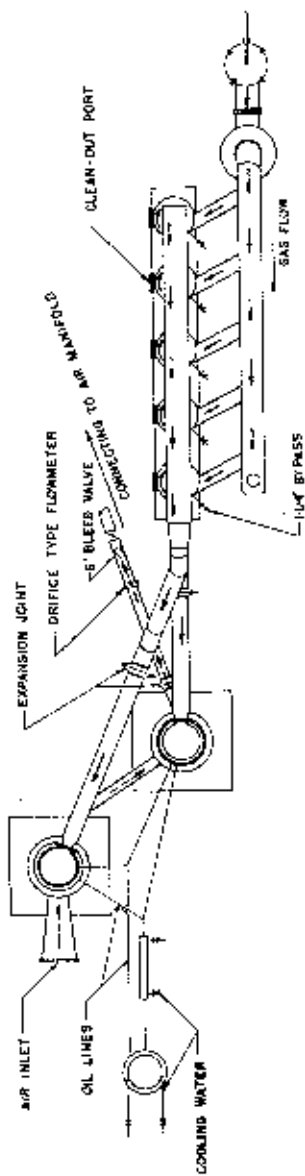
The last operating phase of the experimental installation was to determine if a longer coal face exposed to gas flow would be advantageous. This operation was between boreholes III and V, which provided 600 feet of path, initially bordered by four coal faces. Free oxygen appeared after several cycles, and the calorific value of the gas was low. Material balances show that the amount of coal consumed was equivalent to the entire pillar between the entries plus 10 feet off the sides of the entry in the solid coal. The operating characteristics of the section were similar to those encountered previously. The increased face area at first exposed in this operation increased the rate of coal consumption but had little effect on gas quality. A very long cycle of unidirectional flow resulted in high gas temperatures, with little change in analysis, and greatly increased the fraction of the energy of the coal appearing as sensible heat in the products.

Several periods of low input air rates were made to determine this effect. The generation of steam in both the old and contemporary operating areas caused the results to be inconclusive; the proportion of water vapor in the product gas was high. Lowering the air input rates led to initial increased calorific value of the gas, which was due to the increase in the reaction between steam and coke. Prolonged operation at low air rates was characterized by decreasing calorific value; this was probably due to general cooling of the reacting faces.

In February 1951 operations ceased and flooding of the system with water was started. Cooling has progressed satisfactorily to the present time. The operation at Gorgas has demonstrated that the combustion of coal in place can be extended over a wide area from a single initial passageway in the coal bed, as shown in figure 13. It has been possible to advance a burning face still further into the solid coal by drilling boreholes to intersect the face. The low calorific value of the gas produced was due to incomplete contact between air and coal caused by voids formed in or above the original entries and in the burned out area. These voids allowed the air to bypass the coal faces. Efforts to fill these voids with dry, fluidized solids were only partly successful. Favorable conditions for gasification were obtained when the gas outlet was located very near an incandescent carbon face. The quality of the gas decreased as the reacting face receded from the borehole; increasing pressure, temperature, and gas velocity near the outlet, in the presence of hot carbon, resulted in improved quality of gas.

It was possible to bring a large proportion of the energy of the coal to the surface as sensible heat when desired. An installation, whereby the hot gas is expanded through a turbine, would require gas-tight strata and minimum pressure drop through the system, but many coal beds retain natural gas under pressure, and these beds may fulfill requirements for gas turbine operation.

The most urgent problem in underground gasification is control of the contact between air and coal. With contact assured, gasification will result, and it will be



NOTE: ALL HOT GAS-CARRYING PIPE COVERED WITH 2\"/>

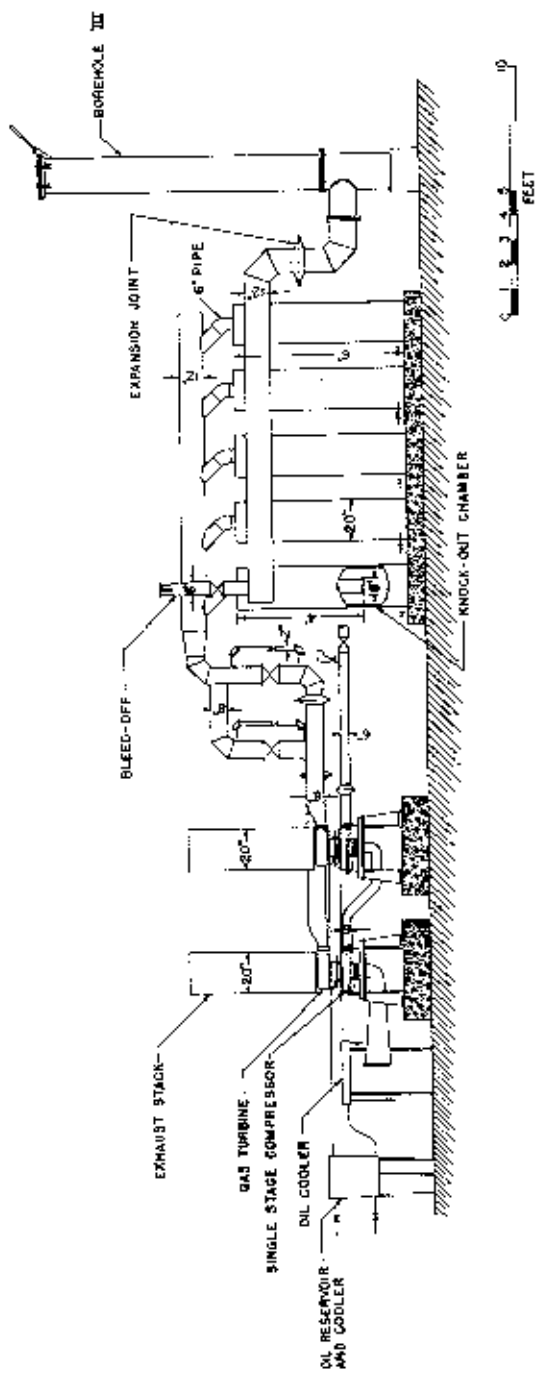


Figure 14. - Gas turbine installation, underground gasification test, Gargas, Ala.





possible to refine the process by further development. Subsidiary problems, such as optimum rates of gasification, control of leakage, methods of underground development, and design of special equipment, can be attacked simultaneously. The operation at Gorgas has revealed much useful information on these problems.

## RESEARCH ON THE PRODUCTION OF SYNTHESIS GAS

### Gasification of Pulverized Coal

#### Laboratory-Scale Experimentation

The development of an easily controlled laboratory process for the continuous production of synthesis gas from powdered coal at ordinary (atmospheric) pressures has been described.<sup>79/</sup> This method, powdered-coal gasification by down-draft entrainment in oxygen and steam, has been considerably standardized after some further development of the feeding system and purification train<sup>80/</sup> and was used to carry out a preliminary program of testing fuels for their relative value in synthesis-gas production.

A flow sheet (fig. 15) shows the 50-pound-per-hour gasifier, pneumatic feeding system, and purification train, with modifications made during the year. These modifications include the substitution of a much larger continuous feeder (10-inch i.d. fluidizing tower) for the former 4-inch diameter vessel and the use of a single batch feeder of the same diameter, as shown in the flow diagram. The dry method of removing dust from the synthesis gas was replaced by two efficient scrubbers and a baffle chamber capable of recovering the bulk of the carbonaceous residual dust, followed by an improved micrometallic filter to remove the last traces of residue.

Gasification runs were, as a rule, voluntarily discontinued after 4 to 5 hours, although some runs of 23 hours' duration have been made and could have been continued indefinitely. Very little slag formation was ever observed on the 7-foot silicon carbide generator tube of 6-inch internal diameter.

The improvements and installation of additional controls have resulted in a greater saving of labor and considerable precision in duplicating the results. The apparatus is capable of gasifying different types of fuels under variously chosen operating conditions at unusually high coal-throughput and corresponding gas-output rates. At feed rates up to 55 pounds per hour, the coal throughput ranged up to 48 pounds per hour per cubic foot of generator volume and the output up to 920 cubic feet an hour of carbon monoxide plus hydrogen per cubic foot of gasifier volume. These operating results and others were found to be functions of the rank (type) and composition (grade) of the coal gasified.

As a result of 79 runs made, it is clearly indicated that low-rank coals of younger geologic age give better results than older high-rank coals when tested under the same conditions in the same gasifier. In general, the completion of gasification, yield of synthesis gas, and thermal efficiency decrease and the oxygen requirement increases with the rank (age) of the coal gasified. However, less-reactive, high-rank and low-grade (high-ash, high-sulfur and low-ash fusion point) coals may also be gasified effectively, with reduction in oxygen requirement, by a suitable choice and combination of process variables and appropriate changes in the generator design. The

<sup>79/</sup> Sebastian, J. J. S., Edeburn, P. W., Bonar, F., Bonifield, L. W., and Schmidt, L. B., Laboratory-Scale Work on Synthesis-Gas Production: Bureau of Mines Rept. of Investigations 4742, 1951, 42 pp.

<sup>80/</sup> See footnote 77.

modifications required include reduction of heat losses, provision for longer contact time and increased mass transfer rate (diffusion), and suitable refractory lining to withstand higher generator temperatures. Thermodynamic and stoichiometric calculations and translations of the results to operations on large commercial scale confirmed these conclusions derived from experimental data.

#### Gasification by the vortex Principle

A progress report<sup>81/</sup> presented the preliminary results of an investigation on the production of synthesis gas from low-cost pulverized coal and steam-oxygen mixtures in a vortex reactor. The basic principles of the reactor design and an illustrative example of their application were given. A method of calculating, a priori, the composition of the make gas for any set of feed conditions was presented and has been checked experimentally.

Subsequent work has shown the performance of the vortex to be vastly improved by changing the geometry of the vortex and by introducing the coal horizontally into the reactor, so that it is thrown into the rotating gas stream in an umbrella-like pattern.

#### Atmospheric Pressure Pilot-Plant Gasifier

During the year test work was continued on the 500-pound-per-hour atmospheric pressure unit previously described<sup>82/83/</sup>. The generator was rebuilt to permit continuous slag tapping, the generator-base construction being modified from time to time to improve the slag tapping, and 10 test runs were made. Effective slag tapping was attained in these tests with oxygen consumption of approximately 320 cubic feet per MCF of CO + H<sub>2</sub> produced, using steam at 1,000° F. In the early tests it has been indicated that extremely fine pulverization of the coal (90 percent through a 200-mesh screen) was probably not required for good gasification results. In these tests, coarser fuel was fed (as coarse as could be handled in the pneumatic feeder) in some of the runs, and the results indicated that the percent of gasification was satisfactory. After run 42 it was apparent that the limit of profitable experimental work had been reached, using the original generator.

Under a cooperative agreement with the Babcock & Wilcox Co., a new generator was designed. The shell was fabricated in its shops, and the construction on the site, including installation of refractories, was done by Bureau personnel. This new unit will make possible further studies of methods of slag removal and reactant feeding. The dust-removal train, previously used, functioned very well, and no major changes have been made in it.

A patent has been issued<sup>84/</sup> covering gasification of pulverized coal with oxygen and steam. Pulverized coal entrained in a stream of oxygen is admitted near the base of a generator through diametrically opposed ports so that the flames impinge on each

<sup>81/</sup> Perry, E., Corey, R. C. and Elliott, M. A., Continuous Gasification of Pulverized Coal with Oxygen and Steam by the Vortex Principle: Trans. Am. Soc. Mech. Eng. vol. 72, No. 5, July 1950, pp. 599-610.

<sup>82/</sup> Strinbeck, G. R., Holden, J. H., Rothenbach, L. P., Cordiner, J. B., Jr., and Schmidt, L. D., Pilot-Plant Gasification of Pulverized Coal with Oxygen and Highly Superheated Steam: Bureau of Mines Rept. of Investigations 4733, 1950, 41 pages. Abs. in Proc. Am. Gas Assoc., 1950, pp. 501-502.

<sup>83/</sup> See footnote 77.

<sup>84/</sup> Newman, I. L. and Donovan, J. E., Apparatus and Method of Gasifying Carbonaceous Material: U. S. Patent 2,516,141, July 25, 1950.

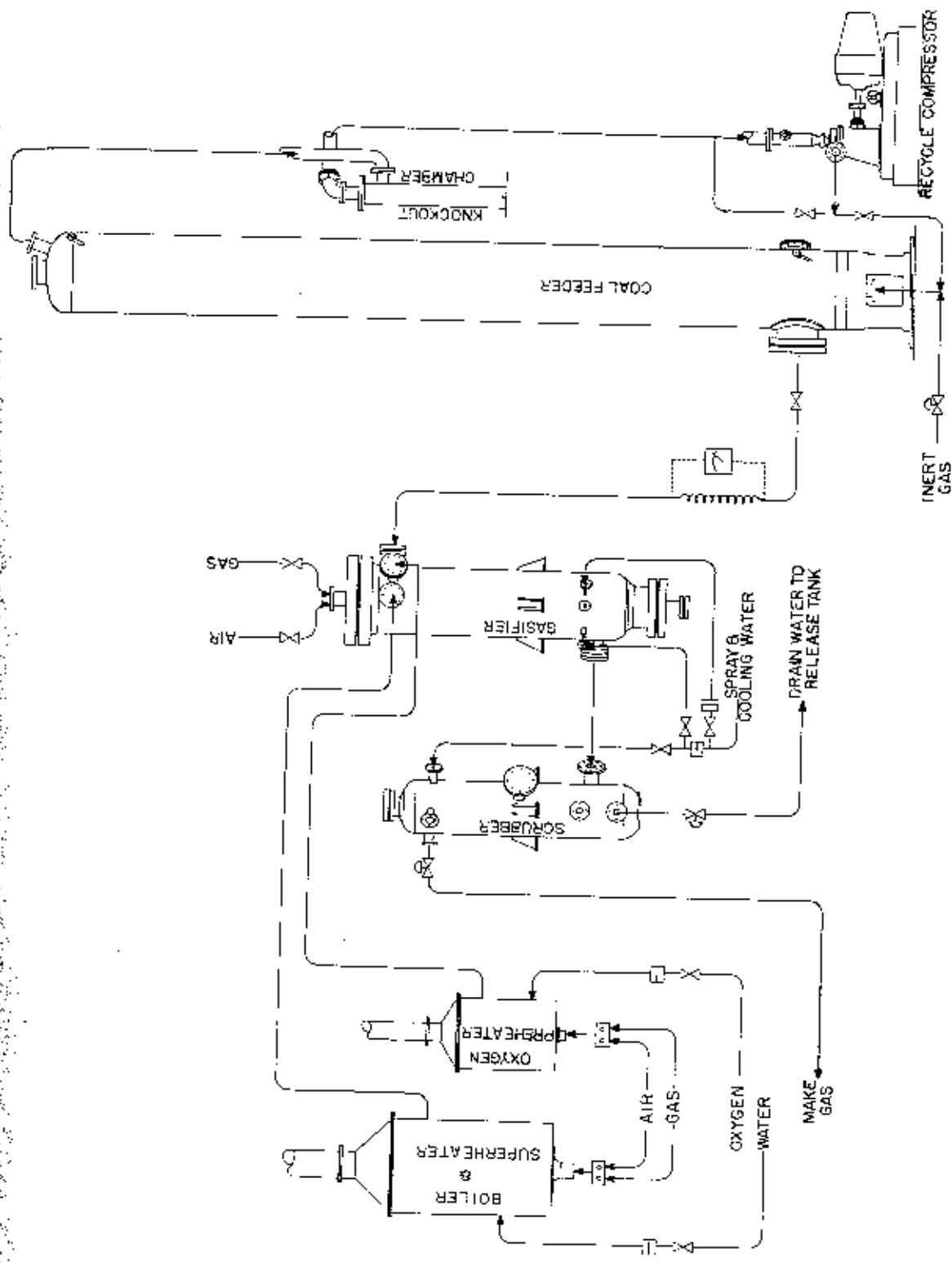


Figure 16. - Simplified flow sheet for pressure gasification.

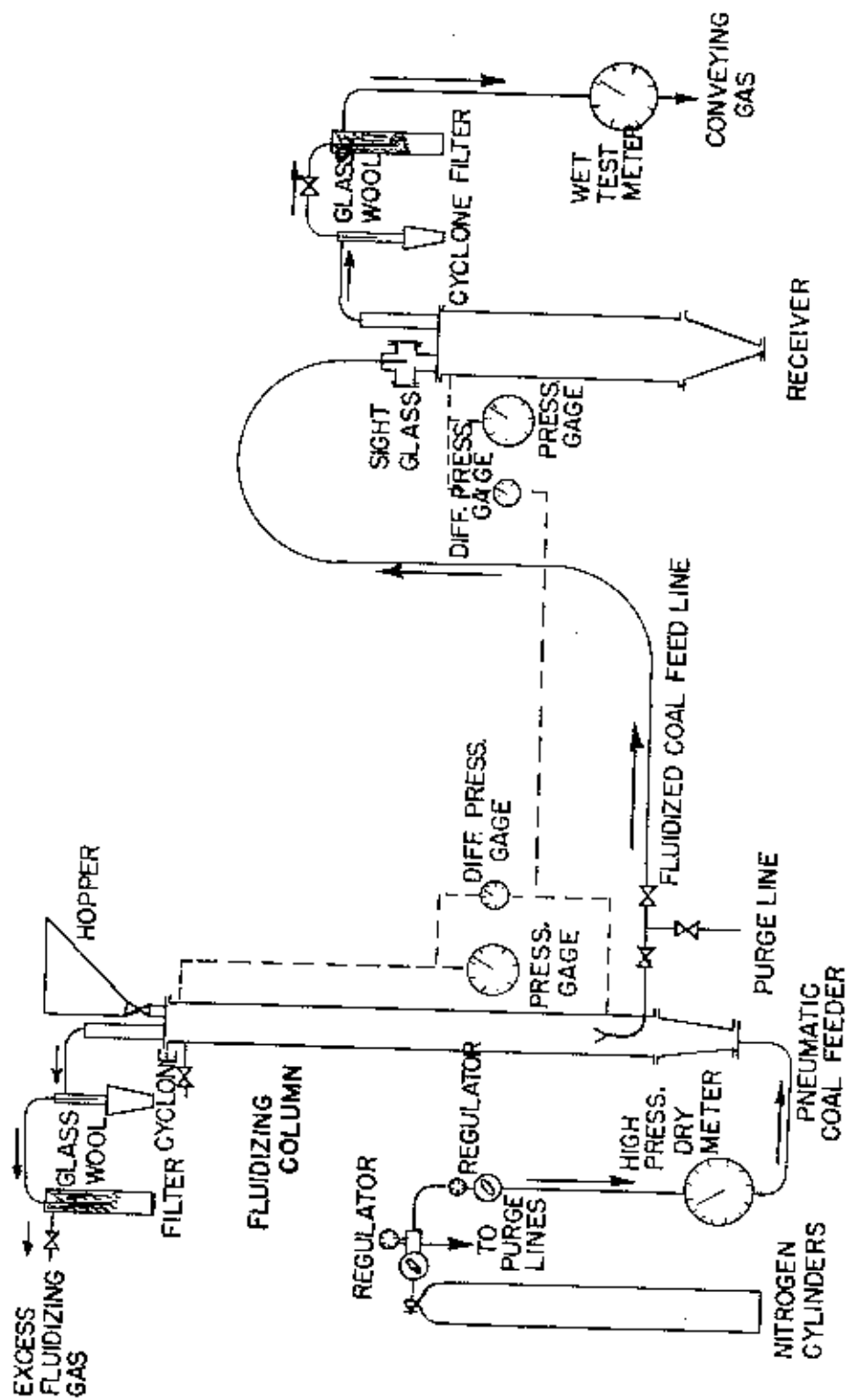


Figure 17. • Apparatus for study of transporting and feeding powdered coal under pressure.

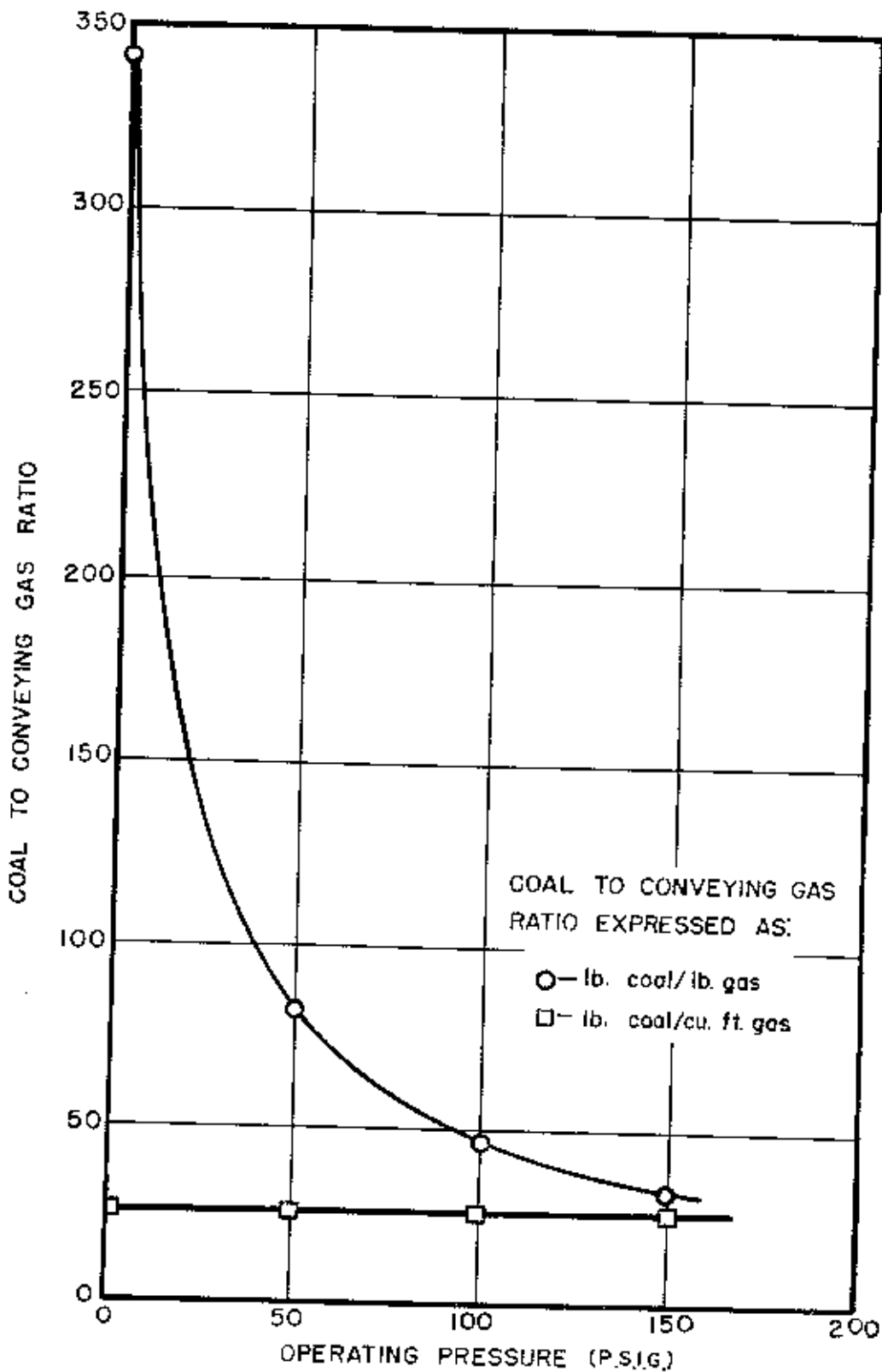


Figure 18. - Effect of operating pressure on the amount of coal conveyed by air or other gases.

other with considerable turbulence. Steam is admitted below the oxygen-coal ports through tangential ports. The process can be used either at atmospheric or high pressures.

### High-Pressure Pilot-Plant Gasifier

The construction of the high-pressure gasification pilot plant<sup>85/</sup> was finished, and test runs were started in June 1951. To date these tests have been of short duration to check the mechanical operation of the various units and to train operating personnel. The performance of the various units has been satisfactory and indicates the correctness of the original design. Figure 16 gives a flow diagram for this high-pressure pilot plant.

Testing an experimental, coke shaft filter has continued. Excellent results in removing very fine dusts have been obtained in the bench-scale apparatus, with low-pressure losses.

### Pneumatic Transportation and Feeding of Pulverized Coal

As the high cost of compression of the synthesis gas, before purification and synthesis to liquid fuels, favors gasification at elevated pressures, a method was developed for the continuous pneumatic transportation and charging of powdered coal into a pressurized gas generator.<sup>86/</sup> Experimental work on a laboratory scale,<sup>87/</sup> under pressures up to 150 pounds per square inch, proved that powdered coal can be transported pneumatically in a dense phase (26 pounds per cubic foot of space in the conveying pipeline) from a fluidized bed and discharged at a constant rate. A flow diagram (fig. 17) shows the apparatus constructed for studying the continuous conveying and feeding of finely powdered coal at superatmospheric pressures.

The results of the experimental work showed that, with other conditions equal, the discharge rate is solely a function of the pressure differential across a conveying tube of given dimensions. It was shown further (fig. 18) that, regardless of the operating pressure, the amount of coal conveyed per unit volume of gas, measured at the existing pressure, is practically constant, but the weight of coal carried per unit weight of conveying gas rapidly decreases with increasing operating pressures. The design information published on pressurized dense phase feeders has not been available heretofore.

### Synthesis-Gas Purification

Of the organic sulfur compounds which may be present in synthesis gas, thiophene is known to be the most resistant to thermal and catalytic treatment. An analytical method using isatin was developed for determining thiophene in gas. With this method, as little as 0.0001 grain of thiophene sulfur per 54.9 ml. of test solution could be detected.<sup>88/</sup> Tests on the gas produced in the first two atmospheric pressure gasifiers showed that no thiophene sulfur was present.

- <sup>85/</sup> Synthetic Liquid Fuels. Annual Report of the Secretary of the Interior for 1950. Part I. Oil from Coal: Bureau of Mines Rept. of Investigations 4770, 1951, 74 pp.
- <sup>86/</sup> Holden, J. H., and Albright, C. W., The Morgantown Fluidized Feeder: Proc. Am. Gas Assoc., 1950, pp. 493-500.
- <sup>87/</sup> Barker, K. R., Sebastian, J. J. S., Schmidt, L. D., and Simons, H. P., Pressure Feeder for Powdered Coal or Other Finely Divided Solids: Ind. Eng. Chem., vol. 43, May 1951, pp. 1204-1209.
- <sup>88/</sup> Walnwright, H. W., and Lambert, G. I., A Colorimetric Method for the Determination of Thiophene in Synthesis Gas: Bureau of Mines Rept. of Investigations 4753, 1950, 11 pages.

A method was developed for continuously determining low concentrations of dust in gas by means of an instrument which compares, by means of photoelectric cells, the intensity of a light beam passing through the dust-laden gas and a similar beam through clean air.<sup>89/</sup> This instrument had a sensitivity of 0.75 grain per 100 cubic feet. The gas-purification research program at Morgantown always contemplated the necessity of including sulfur recovery as a feature of the gas-purification system in any large gas-synthesis plant.<sup>90/</sup> The first gas-purification pilot plant runs were made at 300 p.s.i.g., using 20, 30, 35, and 50 percent aqueous solutions of triethanolamine (TEA) as a selective absorbent for hydrogen sulfide. Data indicate that a 30 to 35 percent solution is the optimum concentration, if both selectivity and economy are considered. Using 35 percent TEA and a raw gas containing about 350 grains of hydrogen sulfide per 100 s.c.f. and 15 percent carbon dioxide, an acid gas containing about 10 percent hydrogen sulfide is obtained. Such an acid gas can be used for sulfur recovery, but not as economically as an acid gas having a higher hydrogen-sulfide content.

Slightly better selectivity is obtained with 20 percent TEA solution, but steam consumption for reactivation is greater, owing to higher solution rates. As a result of the greater solubility of carbon dioxide, a 50 percent TEA solution not only produces an acid gas of lower hydrogen-sulfide content but it also requires high solution rates to effect hydrogen-sulfide removal from the gas.

In cooperation with the Southern Natural Gas Co., investigations were made at 300 p.s.i.g. on the simultaneous removal of hydrogen sulfide and carbon dioxide from gases employing various concentrations of diethanolamine (DEA). Both TEA and DEA reduced considerably the organic sulfur content of the raw synthesis gas. Analyses of the lean amine solutions showed a gradual build-up of sulfur compounds, indicating that the compounds formed by the amines and the organic sulfur do not break down under the ordinary operating conditions of the reactivator. The quantity of steam needed to reactivate fouled TEA and DEA solutions increased as the reactivator pressure was increased. There was considerable difficulty in operating the pilot plant owing to foaming of the amine solutions. Initial additions of anti-foam Alkaterge C agent were successful in reducing the foaming in the pilot-plant absorber, but further additions were less effective.

The potassium-phosphate process for the selective removal of hydrogen sulfide has also been investigated on a pilot-plant scale. Data, thus far, indicate that, with identical gas, this process will give an acid gas containing about twice as much hydrogen sulfide as that obtained with triethanolamine. It is generally thought that the phosphate process is costly because excessive steam is consumed during reactivation, but pilot-plant results have shown this process to be no more expensive than the amine process.

In addition to the removal of hydrogen sulfide and carbon dioxide, pilot-plant runs have been made in which the organic sulfur has been removed from raw synthesis gas with "GW" activated carbon. At present, the activated carbon process for removing organic sulfur appears to be the most economical. If the raw gas entering the carbon purifiers contains about 10 percent carbon dioxide, it is known from laboratory tests that this amount of carbon dioxide in the gas reduces the carbon's capacity for sulfur

- <sup>89/</sup> Stone, D. E., Kane, L. J., Corrigan, T. E., Weirwright, H. W., and Seibert, C. B., Investigation of a Photoelectric Device for the Determination of Low Concentrations of Dust: Bureau of Mines Rept. of Investigations 4782, 1951, 6 pages.
- <sup>90/</sup> Sands, A. E., and Schmidt, L. D., Recovery of Sulfur from Synthesis Gas: Ind. Eng. Chem., vol. 42, November 1950, pp. 2277-2287.



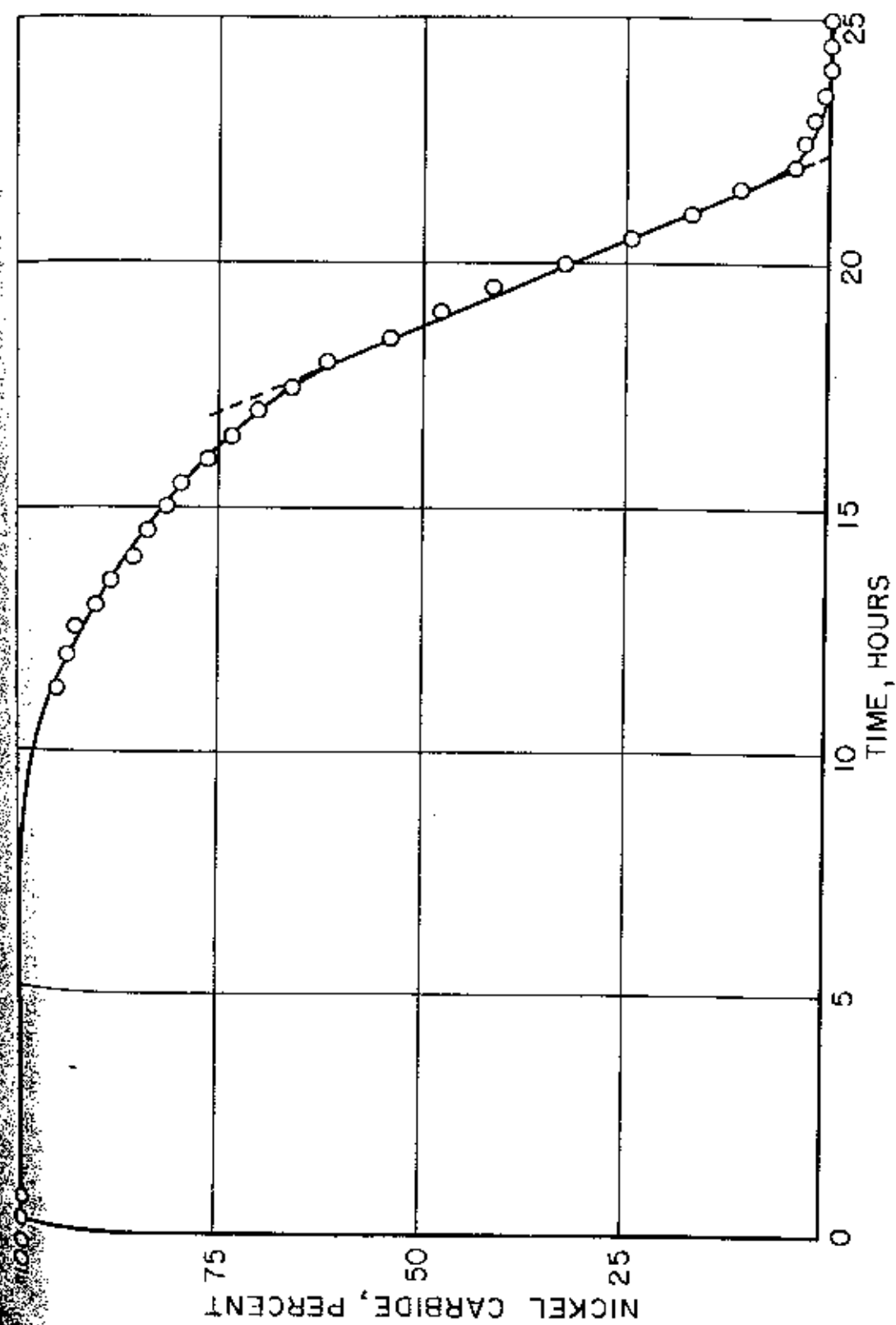


Figure 19. - Isothermal decomposition of fully carburized  $\text{Ni}_3\text{C}$  at  $323^\circ\text{C}$ .