form a naphthalene-type structure; and (6) two six-membered aromatic rings joined together by a single bond to form a biphenyl-type structure. This information indicates that the same complexity of structure apparently persists throughout all classes of compounds in the tar, and that a particular structure found in one class of compounds will likely exist in other classes.

Because of the obvious economic significance of phenols and the relative ease with which they can be separated and analyzed, initial work centered mainly around this class of tar constituents. A list of 183 low-boiling phenols and their physical properties was published.[64]

To study the sorption of individual pyridine bases by cation-exchange resins, an accurate and relatively quick method was needed for determining small quantities of these bases in aqueous methanol solutions.[65] This ultraviolet spectrophotometric method can be applied to dilute solutions of individual tar bases and simple mixtures of tar bases.

Upgrading and Utilization

Low-temperature coal tar is an extremely complex mixture of organic compounds; as such, it has little more than fuel value. To increase its value, the whole tar must be separated into its components, some of which must be converted to substances of greater commercial importance. The upgrading plan comprises a series of selected physical separation processes, such as distillation and solvent extraction, and chemical conversion processes, such as dealkylation and oxidation.

A process for isolating tar acids, employing monoethanolamine as the extractant was reported in 1956. Further laboratory studies of this process resulted in development of an alternative procedure for recovering the tar acids from the monoethanolamine solution. The original procedure used carbon dioxide gas to spring the phenols from the amine solution. The amine carbonate formed in this operation was regenerated by thermal decomposition and reused. The alternate procedure consisted of diluting the amine solution with water and extracting the tar acids with a volatile solvent, such as benzene or butylacetate. This alternate procedure gave a product free of monoethanolamine and eliminated the step of thermal decomposition of the amine carbonate.

Studies on separating neutral tar-oil fractions into chemical types by means of solvent extraction were made. Three selective solvents, furfural, diethylene glycol, and dipropionitrile, were investigated. Of the three, dipropionitrile is a relatively new solvent and has high selectivity for aromatic hydrocarbons. Neutral oils boiling at 200° to 250° C. were separated into aromatic and nonaromatic fractions. The aromatic fraction may be used as a feed material for producing phthalic anhydride, which is of great

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[64] Karr, Clarence, Jr., Physical Properties of Low-Boiling Phenols, a Literature Survey: Bureau of Mines Inf. Circ. 7802, 1957, 15 pp.

[65] Chang, Ta-Chuang Lo, and Karr, Clarence, Jr., Spectrophotometric Determination of Small Quantities of Some Individual Pyridine Bases by Successive Extractions: Anal. Chem., vol. 29, No. 11, November 1957, pp. 1617-1619.

commercial value at present. The nonaromatic fraction, being rich in cyclic compounds, may be used as a blending material for jet fuels. For the same amount of solvent used in single-stage extraction furfural extracted more aromatics than the other two, but the aromatics contained large amounts of nonaromatic hydrocarbons. The reverse was found true for dipropionitrile; that is a product of high quality but smaller in quantity was obtained. Diethylene glycol lay between the two in performance.

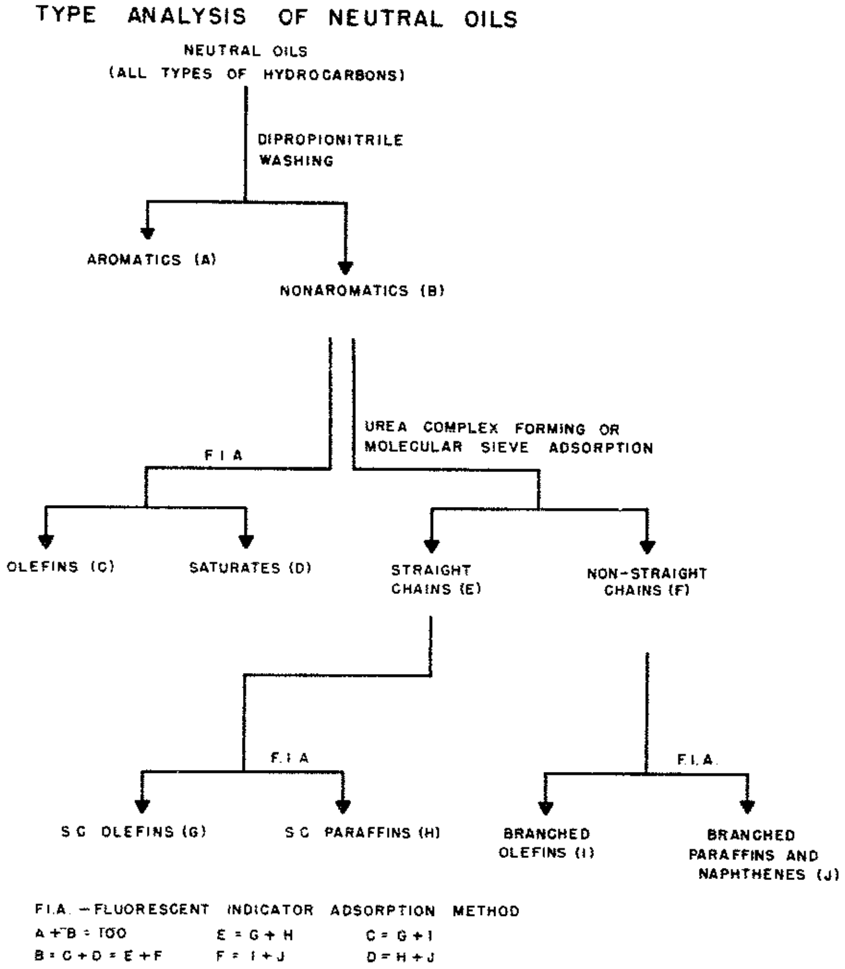

FIGURE 12. - Scheme for Separating Neutral Oils Obtained From Low-Temperature Tar.

An analytical scheme was devised (fig. 12) to separate the neutral oils into five types: Aromatics, straight-chain olefins, straight-chain paraffins, branched-chain and cyclic olefins, and branched-chain and cyclic paraffins. By repeatedly washing with dipropionitrile nearly all the aromatics and the coloring substances can be removed.

As a guide in processing tar acids and tar bases, a comparative study was made of the composition of such mixtures isolated from four low-temperature tars. In these low-temperature tars, tar acids boiling above the range of xylenols represented 75 percent of the total compared with 25 percent for coke-oven tars. The sum of pyridines and quinolines found in these tars was less than 0.5 percent of the whole tar, and the pyridine content was four times as great as the quinoline content.

GASIFICATION OF COAL

Reaction of Carbon With Steam

In gasification of coal the rate is probably limited by the rate of reaction of steam with carbon. Study of the kinetics of this reaction should therefore contribute basic information applicable to the development and design of commercial-scale gasifiers. Two experimental methods have been used to investigate this subject: The falling-particle method[66] and a method in which a carbon sample is suspended from an analytic balance in a furnace maintained at a constant temperature ranging from 1,800 to 2,400° F., the rate of weight loss being a measure of the rate of reaction. Over 200 runs have been made by the second method to study the effect of the velocity of steam through the reactor and the effect of partial pressure of steam in the steam-helium atmosphere at various temperatures.

Because reports in the literature have indicated that the steam-carbon reaction is catalyzed by a strong neutron flux at room temperature or by gamma radiation, hollow graphite cylinders containing a 1-curie source of encapsulated cobalt-60 were suspended from the balance, and the rate of reaction with steam was compared with that of similar cylinders containing no cobalt. A series of runs at 1,000° and 1,500° F. showed that gamma radiation had no effect on the rate of reaction under these conditions.

Hydrogen by Steam-Iron Process

The production of hydrogen by the reaction of steam with iron has been employed commercially on a small scale for many years. The iron oxide produced in the oxidation step is reduced with producer gas for subsequent use in the oxidation step. These reactions are carried out alternately with a fixed bed of iron granules or spheres. As only a surface layer of the iron takes part in the reaction, only a few percent of the iron is utilized. Thus, large reaction vessels are required, and investment costs are high. Operating costs also are high because conversion of the reacting gases is low. To increase the extent of reaction and thus improve the economics of the steam-iron process, use of a fluidized bed of solids is being investigated for the reaction. Iron oxide particles of 20- to 100-mesh size are employed. The raw materials are producer gas and steam. Iron ore, preferably magnetite, is used to replace losses of iron oxide. Producer gas is used for reducing the iron oxide because it is the cheapest gas that can be made from coal.

A 4-foot bed of synthetic ammonia catalyst of 20- to 100-mesh size was used, and the linear velocity of the gas was approximately 0.6 foot per second to maintain fluidization. For a given ratio of solids-to-gas flow the conversion of the reducing gases was increased by increasing pressure. As the solids flow was increased at a constant flow of reducing gas, the conversion increased, but the extent of reduction of the iron oxide decreased. For the 4-foot bed of catalyst employed conversion of the reducing gases ranged from 40 to 70 percent, depending upon the solids-gas ratio. To achieve conversion of the gases and a considerable amount of reduction of the solids, a higher bed of solids is necessary than was used in the pilot plant. The rate of conversion of steam as a function of solids-gas flow during oxidation was similar to that during reduction. However, the rate of oxidation is more rapid than that of reduction. Investigation of rates of reaction in the process is being continued to find the optimum conditions of operation.

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[66] Dotson, J. A., Holden, J. H., Koehler, W. A., Rate of the Steam-Carbon Reaction by a Falling-Particle Method: Ind. Eng. Chem., vol. 49, No. 1, January 1957, pp. 148-154.

Gasification of Lignite

Because of its inherently high reactivity, lignite appears to be an especially suitable raw material for gasification.

Results were published on experiments carried out in a small-scale, externally-internally heated annular retort gasifier.[67] The gasifier, having a nominal capacity of 40 pounds of lignite per hour, was operated to provide information on the effect of temperature distribution and supplementary internal heating with air on gas-production capacity. Results were compared with those from a commercial-scale gasifier of similar design. A crude ammonia synthesis gas with a $(H_2+CO):N_2$ ratio of 2.9 was produced at hourly rates up to 164 cu. ft. per sq. ft. of externally heated surface.

In developing a process for gasifying lump fuel in a fixed-bed gasifier with oxygen and steam at elevated pressure, a pilot plant was designed and contracts for equipment were made (fig. 13). The structural steel framework has been erected, and numerous items were received for the final assembly. Calculations on the thermodynamics of pressure gasification have been completed for both lignite (low-temperature) char and as-received lignite. Conditions for which calculations were made included pressures of 10 to 30 atmospheres and assumed equilibrium temperatures of 1,000° (1,340°) to 1,300° K. (1,800° F.). Oxygen-steam ratios ranged from 0.1 to 1.9 mol. per mol. (2.1 to 39.9 cu. ft. per lb.), depending upon the overall thermal requirements for the reactions considered. High equilibrium temperatures give high (H_2+CO) concentrations in the product gas and relatively low exit-gas temperatures. Provided equilibrium can be approached at the higher temperatures, oxygen-steam ratios of 0.7 to 1.0 mol. per mol. appear favorable for use with char. Somewhat higher ratios can be used with as-received lignite due to the thermal requirements of drying and carbonizing the fuel.

Bench-scale carbonization tests have been completed for evaluating the agglomeration and carbonization characteristics of as-received and steam-dried lignite and subbituminous coal at a controlled temperature of 945° F. and at pressures ranging from atmospheric to 1,000 p.s.i.g. of hydrogen. To evaluate the effect of hydrogen on the carbonization characteristics, experiments were also run in a nitrogen atmosphere under similar test conditions. Agglomeration of feed material was not found to be a problem under conditions expected in the gasifier. Some coke formation was noted with lignite in a hydrogen-rich atmosphere at pressures from 600 to 1,000 p.s.i.g., and maximum agglomeration was at 1,000 p.s.i.g. However, all agglomerates had low mechanical strength and could be crushed easily between the fingers. Lignite agglomerated more than the subbituminous coals that suffered less thermal decomposition and partial hydrogenation. Yields of gas and solid residue followed the general pattern, because more gas was formed at the higher pressures, whereas yield of solid residue decreased. Tar yield was highest at 1,000 p.s.i.g.; at the lower pressures, change was insignificant.

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[67] Oppelt, W. H., Kamps, T. W., Gronhovd, C. H., Kube, W. R., and McMurtrie, R., Production of Crude Ammonia-Synthesis Gas From North Dakota Lignite in an Annular-Retort Gasifier: Bureau of Mines Rept. of Investigations 5297, 1957, 29 pp.

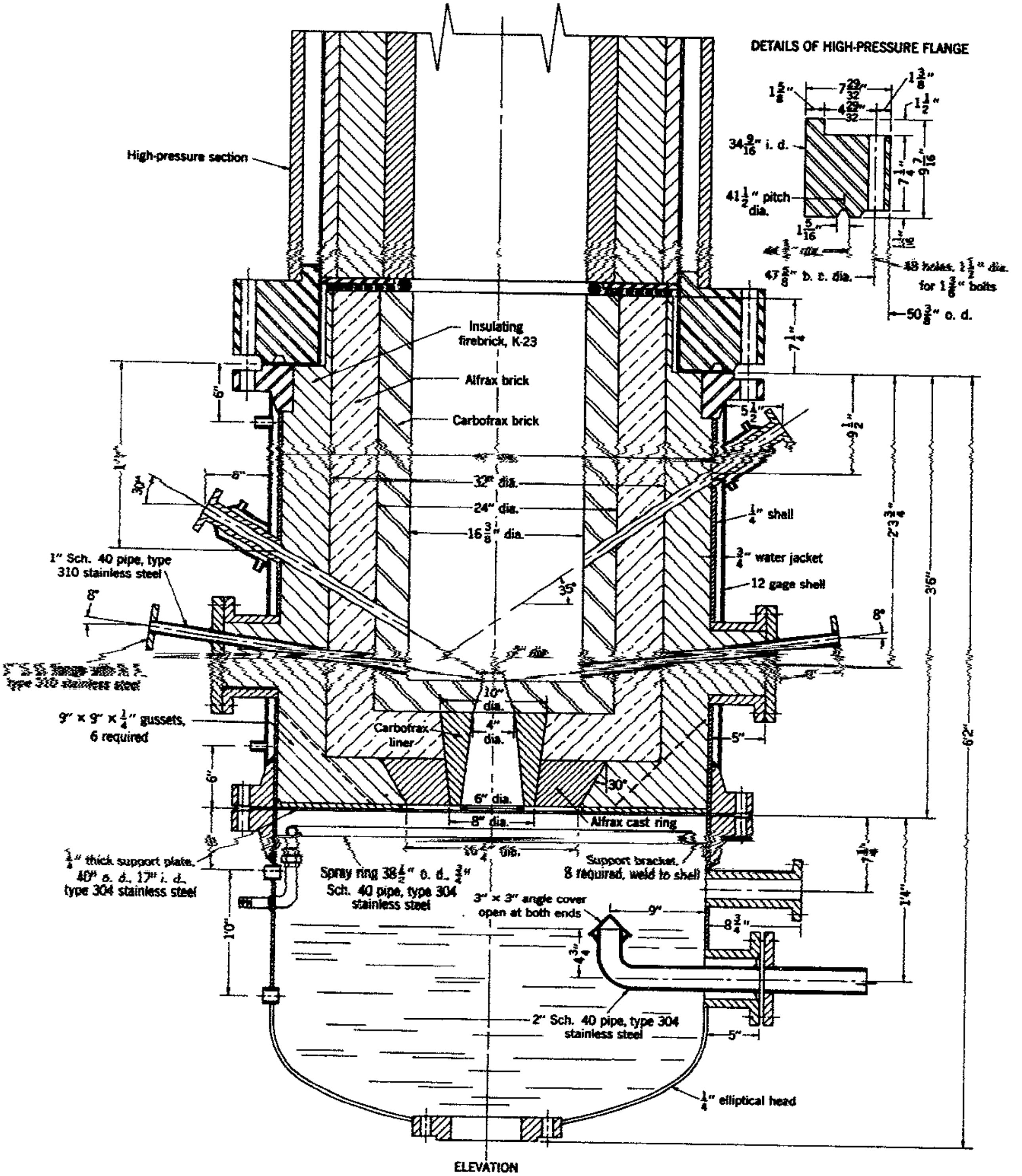

FIGURE 13. - Low-Pressure Slagging Section of Fixed-Bed Gasifier.

Gasification of Pulverized Coal

Pilot-Plant Operation

For several years gasification of pulverized coal to produce gas for synthesis of hydrocarbons, methanol, or ammonia has been studied on a pilot-plant scale.[68] Changes in design have been introduced periodically to improve operations. Recently, a new refractory lining was installed in the reaction zone of the pressure gasifier. It changes the heat conductivity through the lining and permits evaluation of the effect of this variable on gasification.

Coal-Feeding Methods

Work in developing methods of feeding pulverized coal into a pressure gasifier continued with emphasis on a system in which a slurry of 50 percent pulverized coal and 50 percent water is heated to yield a mixture of superheated steam and preheated coal. Preheating lowers the requirement of oxygen, the third medium of gasification. However, before such a mixture can be fed into a pressure gasifier, its steam-coal ratio must be reduced. A suitable steam separator is being developed.

Some work has also been done on a system for feeding steam and coal in which pulverized coal under pressure is inspirated into a stream of steam, which then passes through a heater into the pressure gasifier.

Modification of the fluidized feeder used in the pilot plant from a "single-zone" to a "two-zone" feeder" feeder (fig. 14) allowed lowering the fluidizing gas requirements to 25 percent of the requirements for a single zone. Carryover of particles (coal entrainment) was reduced to a trace and the feeding capacity of the fluidizer doubled.

In this "two-zone" feeder the distribution plate, normally used for fluidization in the large feeder, was altered so that a central column and an annular column could be fluidized at different rates. A central column with a large funnel at the top was placed above the altered plate. In operation, the inner column of coal is fully fluidized, and the coal feeds out through the small funnel and extraction pipe. The annular column is only slightly fluidized. The large funnel forces gas from the annular column to the outer edge of the feeder and assists in feeding the coal from the upper zone down into the small fluidized column.

Externally Heated Reactor

Because gasification of coal by steam is an endothermic reaction, heat must be added to the system to maintain the rate of reaction. In a pressure gasifier the necessary heat is generated internally by adding oxygen that reacts with the coal to the steam required for gasification. Heating the reactor

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[68] Strimbeck, G. R., Holden, J. H., McGee, J. P., and Hirst, L. L., Recent Work by the Bureau of Mines on the Gasification of Pulverized Coal: American Gas Association, Operating Section (Preprint) CEP-55-27, 32 pp.

externally is an alternative method, and about 80 runs in an externally heated coil have demonstrated that gasification of coal-water slurries fed to such a reactor is feasible (fig. 15). The coil was kept at 1,500° F. or above continuously for 1 year, and coal-water slurries were fed through it intermittently for a total time of about 100 hours. The coil was in good condition at the end of this period. The younger, more reactive coals gasified more completely and at a faster rate. Over 90-percent carbon conversion has been obtained with a geologically older (higher rank) lignite from Lake DeSmet, Wyo., at 1,900° F. in less than 1 second residence time. Longer residence times and higher reaction temperatures increased the carbon conversion to gas but had little effect on the gas composition. The average gas composition was 57 percent H_2, 20 CO_2, 15 CO, 4 CH_4, 2 unsaturated hydrocarbons, and 2 percent N_2. A linear relationship was found between carbon conversion and the ratio of steam to coal: The greater the amount of steam present, the more carbon was gasified under similar conditions.

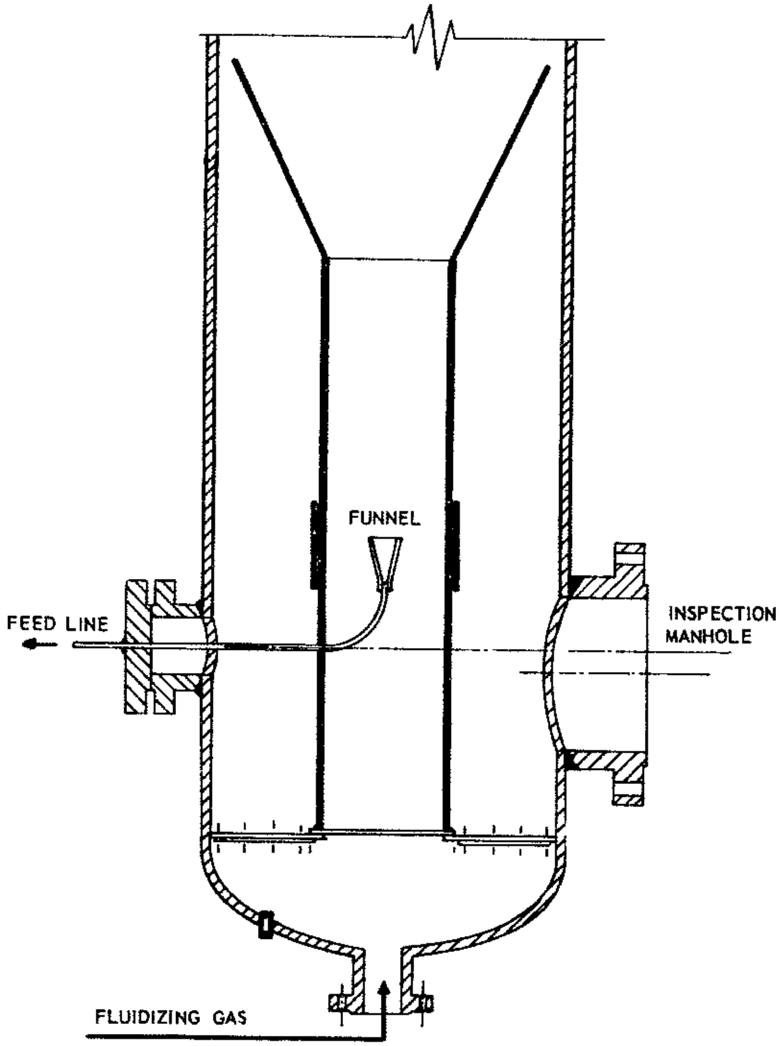

FIGURE 14. - Section of Two-Zone Feeder for Feeding Powdered Coal to a Gasifier.

Nuclear Energy for Coal Gasification

Energy from a nuclear reactor may be used in three ways that are of interest in coal gasification: (1) The energy released as heat may be used directly in a gasification unit to maintain a high rate of gasification; (2) the heat may be used indirectly through some heat-transfer medium to accomplish the same objective; and (3) the energy may be used to superheat steam to such a high temperature that the reactions are self-sustaining.

In 1955 a cooperative program with AEC was initiated to develop nuclear reactor technology to permit heating of gases to 2,500 to 3,500° F. and to investigate methods of applying this heat to a steam-coal mixture so that

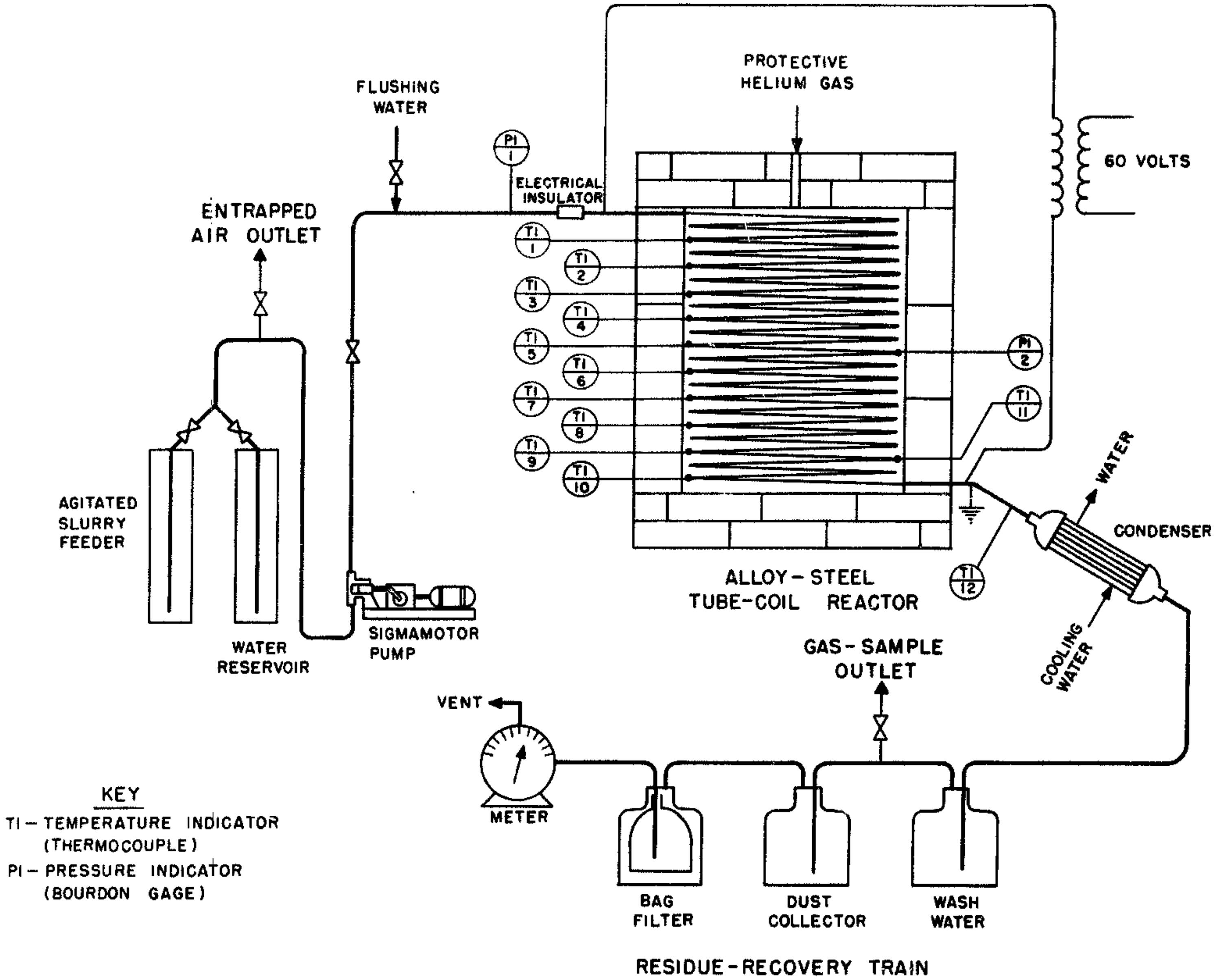

FIGURE 15. - Externally Heated Coil for Gasifying Coal-Water Slurries.

essentially no radioactivity is imparted to the products. Because irradiation tests on coal and coal ash showed that the ash became radioactively "hot," even after 30 seconds exposure, the indirect method was selected with helium as the heat-transfer medium. An alternative gasification process that appeared very attractive was to superheat the steam in a nuclear reactor and then react the steam with coal in a separate unit. To study this problem, a "simulated" nuclear reactor has been built in which graphite spheres heated by induction serve as counterparts for the nuclear fuel elements (fig. 16).

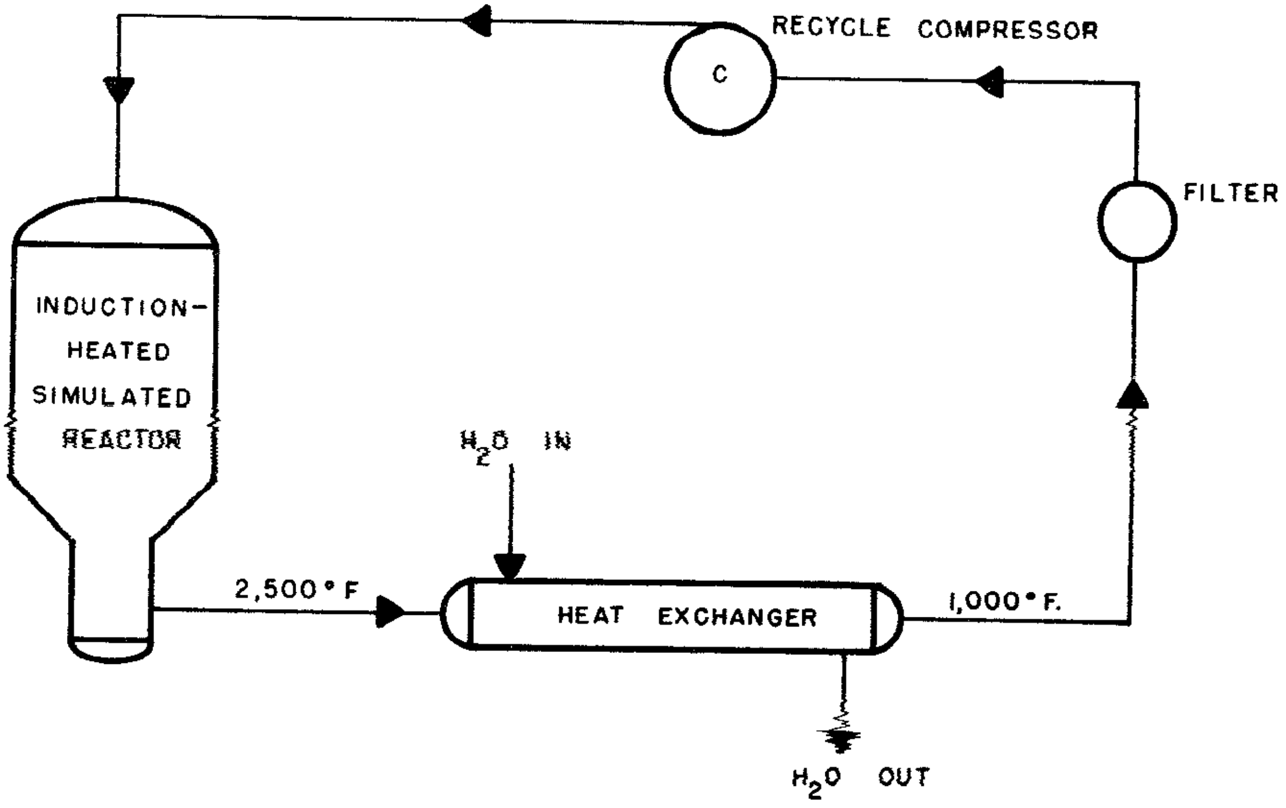

FIGURE 16. - Simplified Flowsheet for Simulated Nuclear Reactor With Helium Recycle.

<u>Heat Transfer</u>

In a first step, this reactor has been used to procure information on heat transfer by helium at atmospheric pressure. The gas is heated to 2,500° F. and cooled in a gas-to-gas heat exchanger to about 1,000° F. Experiments are planned at pressures up to 250 p.s.i.g. Both the compressor and the heat exchanger require development programs. Preliminary designs have been made and a prototype compressor and heat exchanger have been ordered. Some heat-transfer measurements have already been made at low rates of flow of helium because of the low capacity of the compressor used to circulate the helium. Two types of ceramic heat exchangers have been designed for the temperature range 2,600° to 2,800° F. and were fabricated of vitreous alumina. One is a shell-and-tube exchanger fabricated in one piece. The other design permits the installation of thermocouples at 3-inch intervals along the interior tube surface followed by the final cementing of joints in place. This heat exchanger has been in satisfactory operation for 2 months at a variety of flow conditions and at temperatures as high as 2,500° F.

Materials for Construction

Laboratory tests are in progress on materials required for effective utilization of nuclear heat. Material-testing reactors have been constructed to determine properties and reactions of materials at high temperatures. Endurance tests have been made to determine the heat, corrosion, and erosion resistances of various ceramics and cermets. Numerous materials have been tested at high temperatures, but no ideal cladding material has yet been found for coating ball-shaped, graphite fuel elements containing fissionable materials. However, the technical feasibility of using unclad graphite fuel elements in helium at 2,500° F. has been demonstrated under simulated nuclear conditions.

Gasification of Anthracite

For successful operation of the Lurgi gasification process, which operates under pressure with steam and oxygen, only noncaking coals have been satisfactory. Anthracite fulfills these requirements; hence, two tests - one on Chestnut size anthracite containing 27 percent ash and the other on a Rice-Buckwheat mixture containing 19 percent ash - were made at the Dorsten works of Steinkohlengas A. G. in Germany. The tests demonstrated that both samples could be gasified. Although optimum operating conditions could not be determined because of limited oxygen supply and because it was necessary to maintain the producer in satisfactory operating condition at all times to provide gas for an international gas grid, reliable data within these operating limitations were obtained. The highest throughput rate obtained was 273 pounds of coal (dry basis) per square foot per hour or 199 pounds per square foot per hour on a dry, ash-free basis. In general, as the throughput rates increased, the carbon-conversion rate decreased; hence, the combustible residue in the ashes increased with the higher rate, owing, primarily to the limited oxygen supply and the large amount of steam used for the operation. Bureau of Mines observers agreed with the Lurgi engineers that certain changes would have to be made to the gasifier to take advantage of the high ash-fusion temperature of anthracite.

Underground Gasification

Experiments in underground gasification of coal are in progress to develop methods whereby chemical products or thermal energy from unmined coal may be brought to the surface. Such a method might permit utilization of coal in beds that cannot be profitably mined or of coal that remains in areas where mining operations have been completed.

The tests completed have been conducted in Alabama in the America coalbed, which is double bedded, heavily cleated and about 5 feet thick, including 10 to 11 inches of fire-clay parting. A permeable path is developed by hydraulic fracturing and injection of fluids in the coalbed. This path is connected to air and gas piping on the surface by boreholes. Gasification paths are then developed between the boreholes by a procedure called "backward burning," in which the coal is ignited some distance from the air-injection hole, and partial combustion then proceeds in a comparatively straight line toward the point of air injection until the path is linked by a partly devolatilized and relatively permeable mass of coal. Then the air flow is reversed and gasification of the coal occurs.

In the most recent hydraulic fracturing experiment the primary objective was to propogate and extend a fracture in the coalbed by means of water loaded with larger sand grains than had been used in the first experiment, in which kerosine and finer sand were tried. During postfracture permeability testing, it was discovered that the inflow and outflow capacities of the boreholes (except the fracture injection borehole) could be increased significantly by injecting 100 to 1,000 gallons of water. This suggested that, properly applied, small amounts of water might eliminate the expense of using equipment for injecting large amounts of fluid and sand.

Gasification operations and results in this second fracturing experiment were similar to those previously obtained. The quality of gas produced initially reached a maximum of 170 B.t.u. per cu. ft. In the following 2-week period the gas quality varied between 100 and 120 B.t.u. per cu. ft. During the next 2-week period the gas quality gradually declined to 50 B.t.u. per cu. ft.

A series of small-scale electrolinking tests in the Pratt coalbed at a nearby site were completed in September 1956 and included seven trials in which vertical electrodes were used similar to those used in the large-scale work.69/ Six of these linkages were exposed by mining operations during July 1957. Figure 17 shows the type of linkage obtained - generally cylindrical, about 7 inches in diameter, and not straight. It contained slag or dense coke in the center that changed gradually to a soft coke at the perimeter. Numerous radial and horizontal cracks or fissures in the linkage allowed air or gas to pass from one end to the other. The measured length of the linkage and the time of carbonization were related to the time required for linking and the power consumed during carbonization.

Gas Purification

Commercial utilization of gas made from solid fuels is possible only when the components are in a suitable ratio and when the gas is relatively free of such impurities as carbon dioxide, sulfur compounds, and solids. Naphthalene may also be troublesome.70/

69/ Elder, James, L., Fies, M. H., Graham, Hugh G., Capp, John P., and Sarapuu, Erich, Field-Scale Experiments in Underground Gasification of Coal at Gorgas, Ala. Use of Electrolinking-Carbonization as a Means of Site Preparation: Bureau of Mines Rept. of Investigations 5367, 1957, 101 pp.

70/ Kane, L. J., Gentile, J. J., Trostle, K. E., Katell, S., and Shale, C. C., Turbidimetric Determination of Naphthalene in Gas: Bureau of Mines Rept. of Investigations 5368, 1957, 12 pp.

Removal of Gases

When coal is gasified with oxygen and steam to produce a mixture of carbon monoxide and hydrogen, a considerable quantity of carbon dioxide is formed, along with smaller amounts of hydrogen sulfide and carbonyl sulfide from the sulfur in the coal. Because Fischer-Tropsch catalysts are poisoned by an extremely small amount of sulfur and their activity is impaired by high concentrations of carbon dioxide, these impurities must be removed before synthesis.

FIGURE 17. - Section of Coal Carbonized Underground During Electrolinking.

Purification of synthesis gas by conventional processes is expensive. Purification by a hot solution of potassium carbonate at elevated pressure has been under study in a pilot-plant unit. Because absorption takes place at an elevated temperature, no heat-exchange equipment is necessary between the absorption and regeneration steps, as in the conventional processes.