

Figure 10. - Apparatus for pyrolysis of bituminous coal.

Carbon-Oxygen Linkages

Knowledge of the nature of the carbon-oxygen linkage in coal is essential for understanding hydrogenation and pyrolysis reactions of coal. Mild oxidation of a bituminous coal with air can destroy its coking properties and markedly modify the distribution of products obtained upon pyrolysis. Previous laboratory work in this field has been mainly an attempt to assess, in small-scale equipment, the effect of weathering of coal on the yields of valuable byproduct chemicals from full-scale coking operations. The effect of oxidation by air was studied to determine whether differences in elemental elimination during the pyrolysis of oxidized and unoxidized coal might yield clues as to the type of carbon-oxygen bonds present, since the bonds formed on oxidation probably do not react in the same manner as the bonds originally present.

The apparatus (see fig. 10) used in the pyrolysis experiments was designed to handle small (5-gram) samples of coal. Samples were placed in an Alundum thimble within a Vycor tube, the system was evacuated to about 1 mm., and the furnace was then rolled over the Vycor tube. Water and small amounts of oil were collected in a cold trap, and gas samples were analyzed by the mass spectrometer. Mass balances were established for coke or char, water, gas, tar, and oil. Carbon, hydrogen, and oxygen distribution in the products also were determined. Mild oxidation of bituminous coal markedly modified the distribution of products obtained by pyrolysis. The semiquantitative analysis of the distribution of products from pyrolysis of coal treated at two temperatures showed that mild oxidation appears to facilitate removal of oxygen originally present in the coal. A possible explanation is that molecular oxygen attacks an ether linkage.

X-ray-Diffraction Studies

To understand the structure of coal, diverse methods of high precision must be applied to its study, such as Debye-Scherrer and small-angle-scattering x-ray techniques; replica and transmission electron microscopy; and magnetic techniques. Bruceton anthraxylon appears to consist of a heterogeneous mixture of two constituents, each of which produces its own diffraction pattern. One constituent consists of turbostratic, graphitelike crystals, stacks of large aromatic molecules not too different from sheets of graphite.

Graphite-like nuclei are indicated by the presence of all of the reflections expected from the crystallographic planes of turbostratic graphite in approximately the proper positions. These stacks are about 16 to 17 Å in diameter and about 15 to 17 Å high. This means that the sheet of fused benzene nuclei in these crystallites is about 7 benzene nuclei in diameter, and the sheets are stacked about 5 deep. Simple groups, like methyl, attached to the periphery of the giant molecule provide enough hydrogen to account for the known carbon-hydrogen ratio. In addition to these crystallites, the structure contains another constituent that shows a scattering halo of almost identical diameter with the interplanar spacing (4.7 Å) of aliphatic liquids. This is the γ band of H. L. Riley.^{1/}

The presumption is that the γ band is the result of aliphatic constituents of coal that are in the same disordered state as in a liquid hydrocarbon. The molecules of this aliphatic liquid in coal may not be free but may be attached to the periphery of the graphite-like molecules. From the breadth of the γ band the dimensions of the crystallites may be calculated; they are very nearly the same as the dimension of normal heptane.

^{1/} Blayden, H. E., Gibson, J., and Riley, H. L., An X-ray Study of the Structure of Coals, Cokes, and Chars. The Ultrafine Structure of Coals and Cokes: BCURA, London 1944.

Another type of liquid as well as gas structure^{2/} has been found with Bruceton and Huntington low-volatile, bituminous anthraxylons by means of a newly designed small-angle camera (see fig. 11). Bruceton anthraxylon has the gas-type structure consisting of micelles of about 14.6 Å diameter suspended in some other medium. This value agrees with the crystallite size of coal determined by line broadening. The Huntington County, Fulton bed, low-volatile, bituminous anthraxylon has the liquid-type structure; the distance between layers of crystallites is 20.5 Å. Thus, the micelle size of both coals is essentially the same. This is to be expected if micelle size is identified with crystallite size which is known to be relatively constant over a wide range of rank.

The results obtained are preliminary; application of additional corrections and refining of techniques may modify these results.

Analytical Methods

Polynuclear compounds containing 4 to 10 rings constitute an important portion of the so-called heavy-oil letdown (H.O.L.D.) in the coal-hydrogenation process. The composition of this material is being investigated, not only because of the possibility of securing valuable chemicals from it but also to find means of preventing an accumulation of nonreactive polynuclear compounds in H.O.L.D. that may lead to operating difficulties. Furthermore, H.O.L.D. almost certainly contains several compounds that can produce cancer in experimental animals. The usual techniques for separating and purifying most organic compounds are difficult to apply to the types of compounds found in H.O.L.D., because of their tendency to form solid solutions, which interferes with crystallization, and because of the difficulties encountered owing to the high melting points of the polynuclear hydrocarbons. In an experiment with a "model" mixture, two closely related polynuclear hydrocarbons, fluoranthene and chrysene, were separated by application of a codistillation procedure to molecular distillation. The technique appears to have general applicability, and the program will be continued to ascertain the major components of H.O.L.D. The method can also be applied to Fischer-Tropsch residuums, and these portions of the Fischer-Tropsch oils may thus be characterized.

A radiochemistry laboratory has been established to utilize radiocarbon for studying synthetic fuel processes and for analyzing the products of these processes. Radioactive tracers are a powerful tool for solving certain chemical problems, which, in the past, either could not be solved or would have been very time consuming. One promising use of radiocarbon labeling is in the analysis of the complex products from the coal-hydrogenation and Fischer-Tropsch processes. Quantitative analysis for certain components is virtually impossible by conventional analytical methods. The isotope dilution technique involves addition of a known compound containing C¹⁴ to the mixture and subsequent removal of a small portion of this compound. From the decrease in radioactivity, the original concentration of this compound in the mixture can be computed. Preliminary experimentation is in progress to insure accurate results and to avoid hazards to health. Apparatus for determining the concentration of C¹⁴ is shown in figure 12.

Design and Construction of Instruments

As part of the engineering program, special instruments have been designed and built, and commercial equipment has been modified to meet the needs of various projects (see fig. 13).

^{2/} Riley, D. P., The Low-Angle Scattering of X-ray by Various Coals. The Ultrafine Structure of Coals and Cokes: BCURA, London 1944.

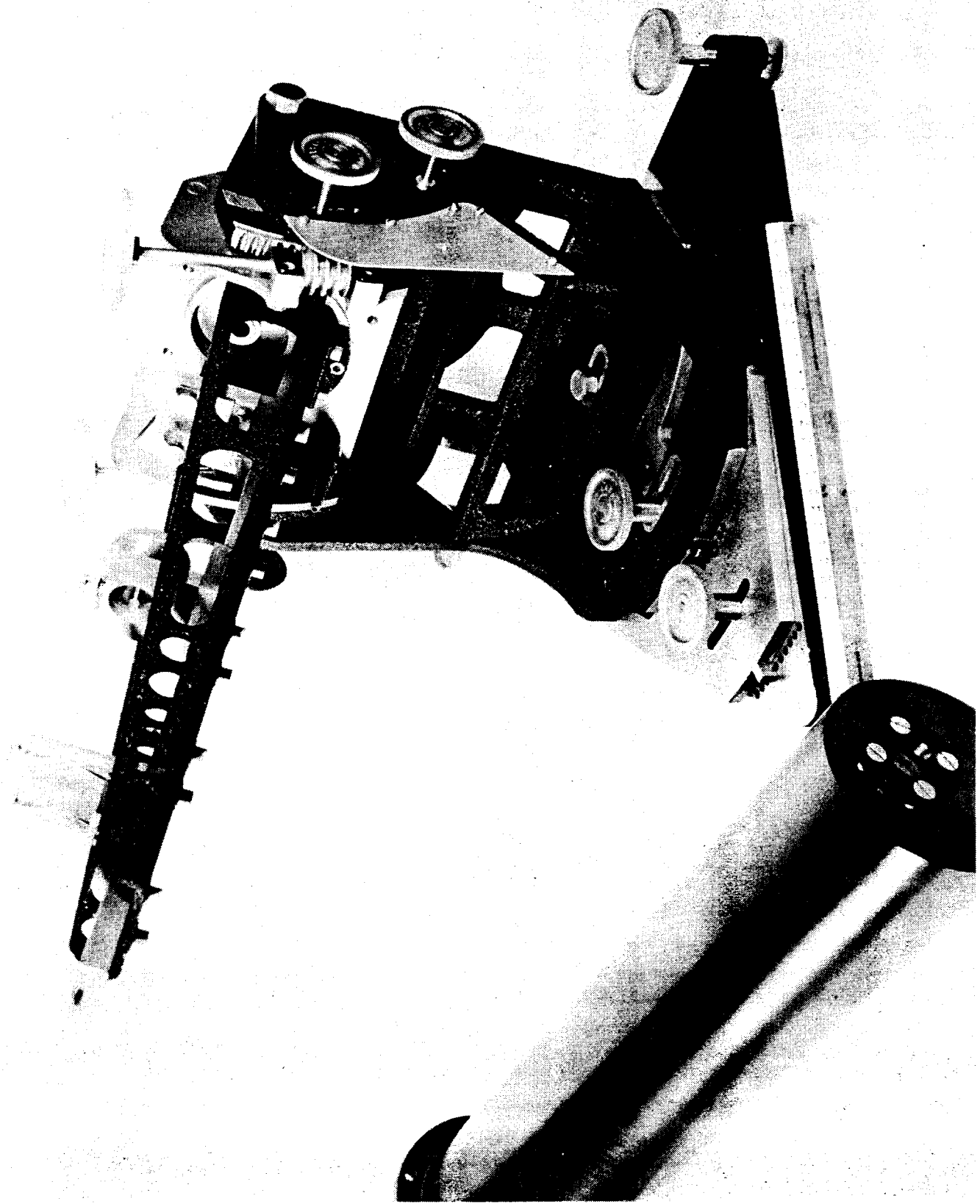


Figure 11. - Small-angle X-ray diffraction camera.

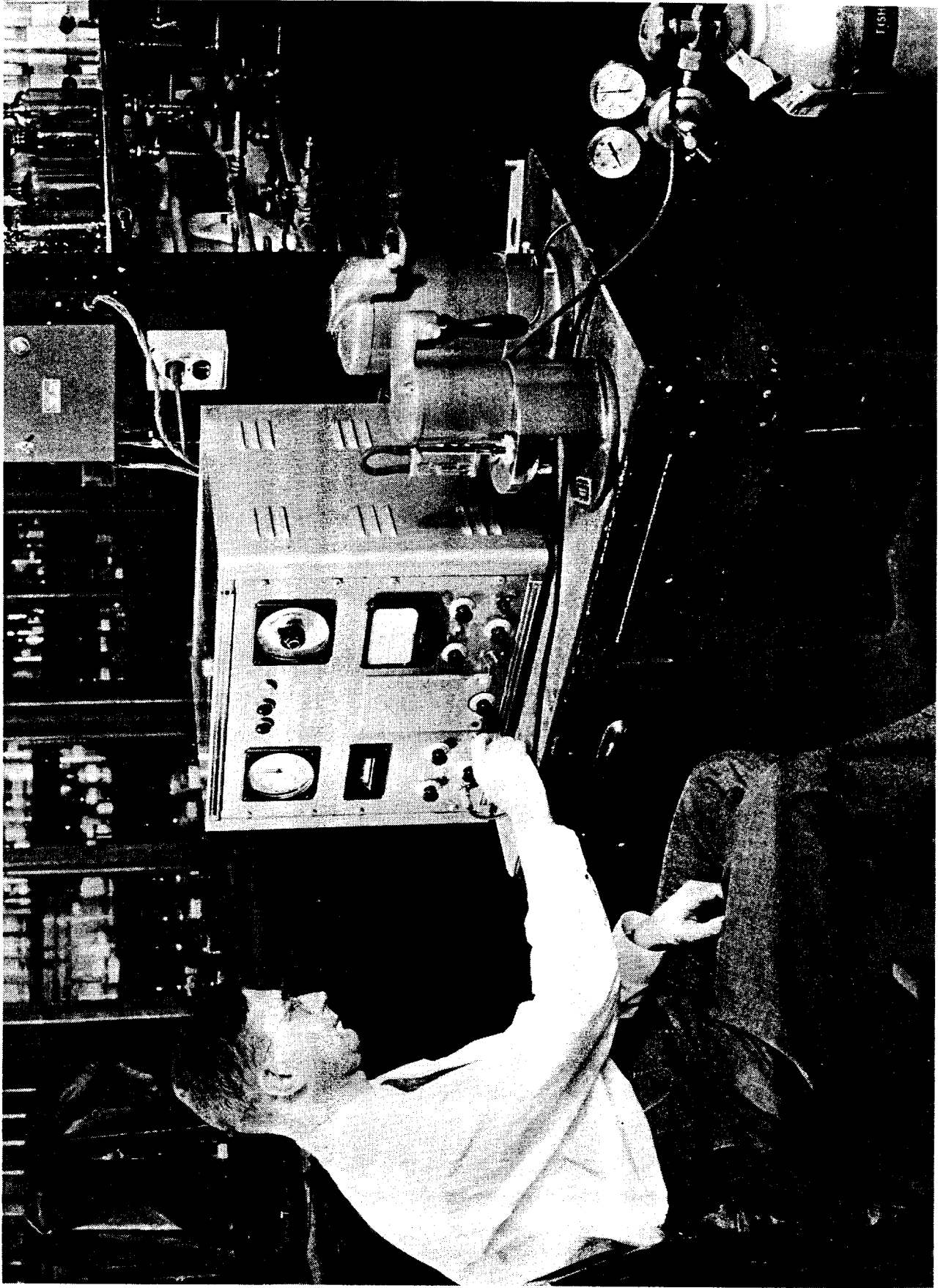


Figure 12. - Scales for measuring activity of radioactive samples.

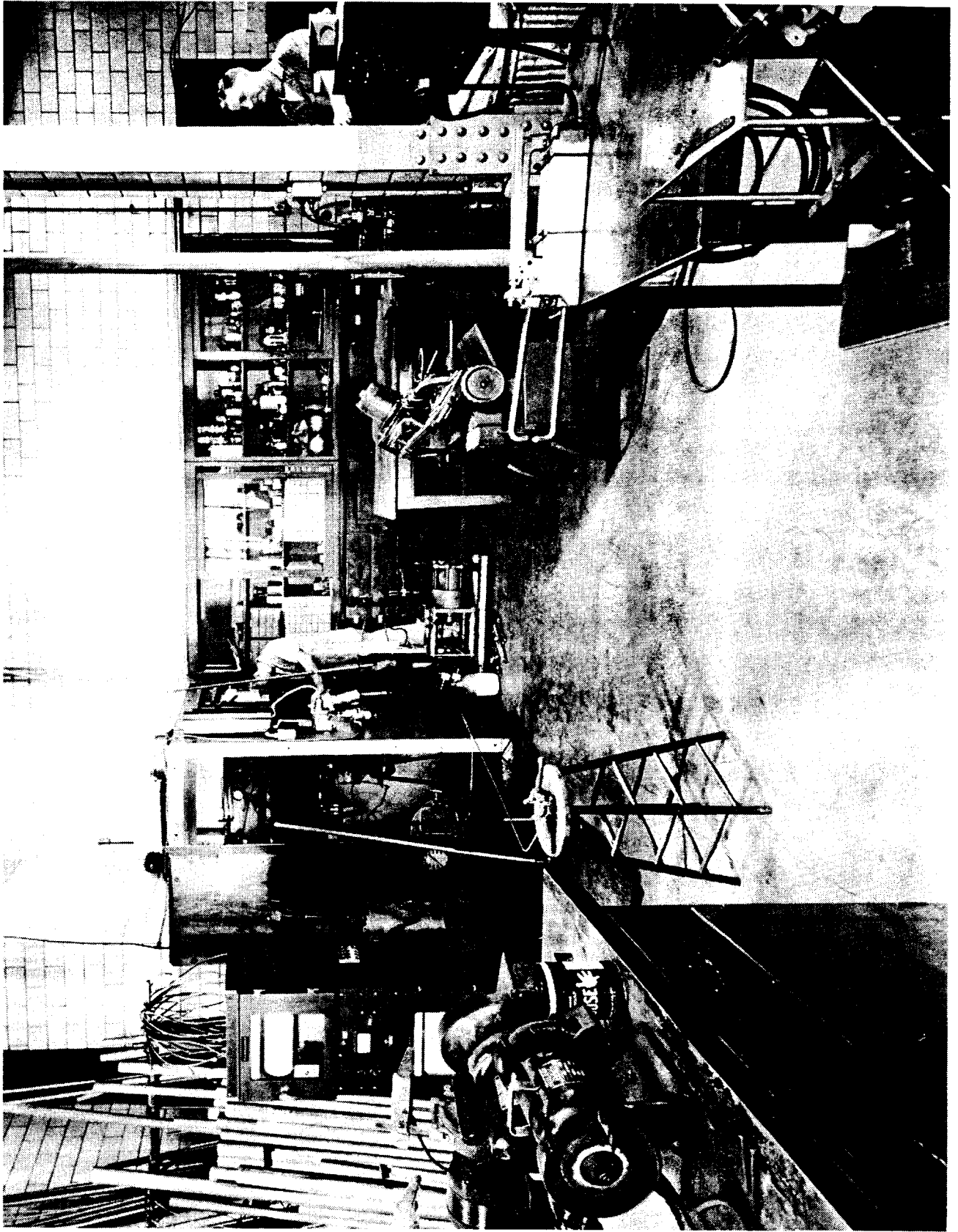


Figure 13. - Equipment development laboratory.

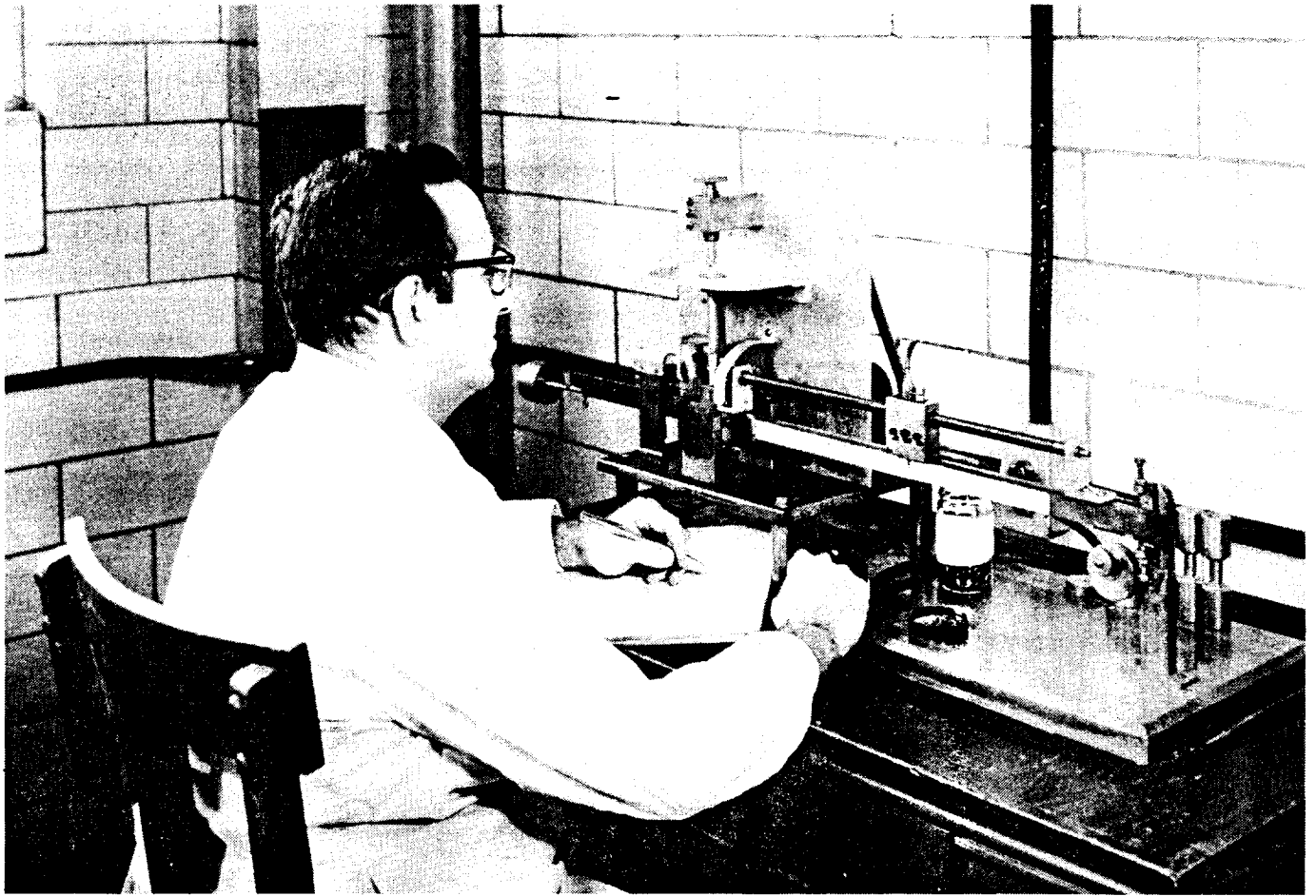


Figure 14. - Testing catalyst pellets for crushing strength.

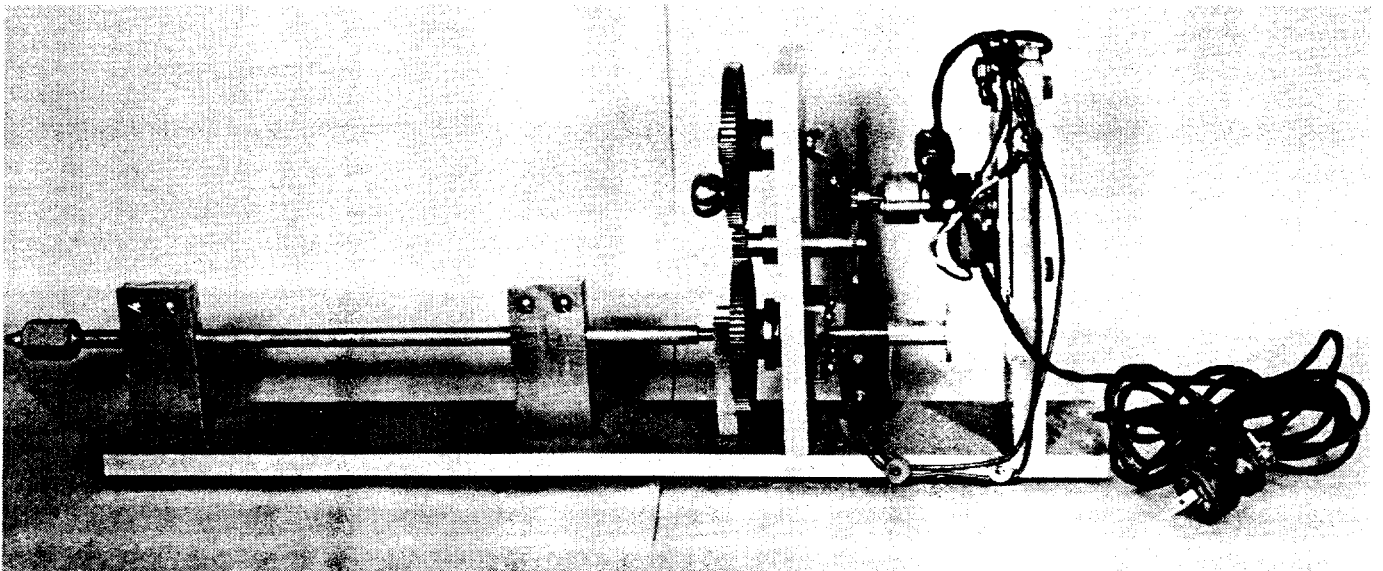


Figure 15. - Pump for injecting liquids into reactors.

Pellet-Strength Tester

An instrument that can give reproducible results in measuring the compressive strength of cylindrical pellets has been developed for testing vapor-phase-hydrogenation catalysts (see fig. 14). The apparatus can test pellets of various sizes. A maximum load of 60 pounds may be applied to a pellet, and the point of failure can be determined within 1 ounce. The pellet is loaded between flat, parallel anvils that apply the load to the sides of the cylinder to measure the strength of the pellet in a direction perpendicular to the axis. The upper anvil is adjustable for different sizes of pellets but remains fixed during a test. The lower anvil is forced against the pellet by a graduated beam along which a weight is moved at a constant rate by a small, synchronous motor. The pellet is subjected to a gradually increasing load until at failure, the beam drops; this motion stops the motor, and the result may be read from the graduated beam.

Slow-Rate Liquid Injector

To add small quantities of liquid at a constant rate to systems operating at 60 to 300 pounds per square inch pressure, injectors (see fig. 15) were developed that operate at rates varying from 1.5 to 10 or more cc. per hour for at least 4 hours. Essentially, an injector consists of a piston moving at a constant rate in a long cylinder. Development of special packing for the piston solved a similar problem involving gas injection.

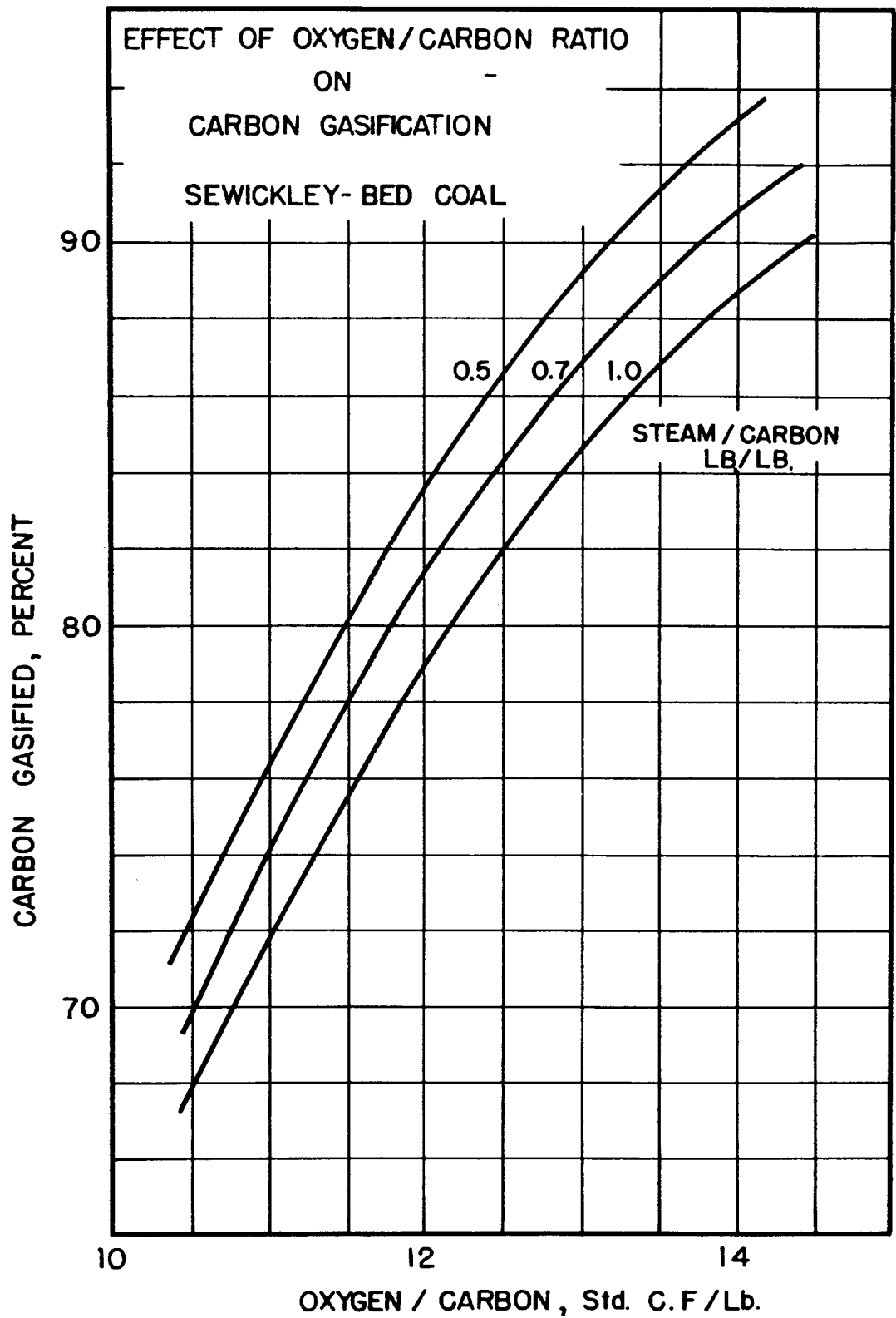


Figure 16. - Effect of oxygen-carbon ratio on carbon gasification of Sewickley-bed coal.

SYNTHESIS GAS FROM COAL PILOT PLANTS, MORGANTOWN, W. VA.

Experimental Development of Processes for Producing Synthesis Gas From Coal

The cost of producing synthesis gas, consisting essentially of carbon monoxide and hydrogen, is a large item in the end cost of such synthetically manufactured products as gasoline, alcohol, ammonia, or pipeline gas. The work of the Bureau of Mines at its Morgantown, W. Va., station has been that of an intensive development program to obtain practical processes that will lower the cost of manufacturing this synthesis gas directly from coal. During the past year work on the atmospheric-pressure gasifier has reached the point where the design of practical large-scale units is possible.

Investigation of the gasification of pulverized coal in the pressure range 300 to 450 p.s.i.g. is continuing. The results have demonstrated the promise of this process, as stated in the 1952 Annual Report. Large capacities per unit of volume of reaction space can be obtained. To develop the process further, a study of various methods of feeding pulverized coal to gasification equipment is in progress.

Atmospheric-Pressure Gasifier

The atmospheric-pressure gasifier was described in the 1952 Annual Report. During 1953, 56 tests were made. One test, using Sewickley-bed coal, lasted 259 hours. Coals from Kentucky, Wyoming, and Washington and a Pennsylvania anthracite also were gasified. Some results using five coals of different ranks are shown in table 2. Analyses of the coals are given in table 3. The data, although insufficient to permit accurate assessment of the different types of coal best suited for gasification purposes, indicate decreased oxygen requirements per unit of product (carbon monoxide and hydrogen) for low-rank coal, such as that from Lake DeSmet, Wyo.

As a result of this and other work, application of this process industrially, under certain conditions, has been shown to be feasible. One chemical company has announced construction of a large-scale gasifier embodying many features developed by the Bureau of Mines in its atmospheric-pressure pilot plant at Morgantown, W. Va. This pilot plant is operable with coals whose ashes have a large range of fusion temperature. Using lower rank fuels, for example, lignites, the gasifier has been operated, with economical requirements of raw materials, nonslagging as well as slagging.

The effect of the oxygen-carbon ratio on the percentage of carbon gasified in the atmospheric gasifier ⁴, using Sewickley-bed coal, is shown in figure 16 for 3 steam-carbon ratios. The cost of raw materials (oxygen and coal) per 1,000 cu. ft. of product (carbon monoxide and hydrogen) may be determined by combining a material balance with results given in this figure for the range of operating conditions (oxygen-carbon and steam-carbon ratios) shown. The range of oxygen-carbon ratios which give minimum requirements of raw materials is about 11.5 to 13.5 cu. ft. per lb. Over this range, there is essentially no variation of materials cost with variation in the oxygen-carbon ratio; that is, as the oxygen-carbon ratio is increased, the coal requirement decreases, but the oxygen requirement increases to such an extent that the raw materials cost is virtually unchanged. The raw materials cost decreases as the steam-carbon ratio is decreased, the lowest materials costs being obtained at the lowest steam-carbon ratios used in these tests. However, at low steam-carbon ratios, the gas is low in hydrogen, and refractory life is shorter, so that a balance is required between hydrogen concentration, refractory life, and cost of raw materials to produce the lowest cost synthesis gas.

TABLE 2. - Some results of operation of atmospheric gasifier 4

Run No.	34 Q	44	42 B	54 I	47 B
Type of coal	Sewickley, W. Va.	Roslyn No. 3, Wash.	Fries, Ky.	Lake de Smet, Wyo.	Anthracite, Pennsylvania
Duration of run	10.0	4.0	2.0	3.0	3.5
Raw-coal rate	466	521	564	613	433
Carbon input	328	365	346	356	356
Process steam-inlet temp.	578	915	925	928	106
Process oxygen-inlet temp.	578	71	45	68	67
Coal-inlet temp.	292	286	275	242	310
Oxygen input per pound of coal	8.80	9.13	8.01	7.41	10.94
Oxygen input per pound of carbon in coal	12.50	13.02	13.08	12.77	13.16
Steam input per pound of coal	.77	.22	.36	.065	1.04
Steam input per pound of carbon in coal	1.10	.31	.58	.11	1.26
Product-gas analysis (corr. for inert gas introduced with coal) percent:					
CO ₂	17.8	7.4	13.6	8.0	21.8
Illuminants	.5	.4	.4	.6	.4
H ₂	40.2	36.8	34.9	33.2	35.0
CO	40.0	54.1	50.2	56.9	41.3
CH ₄	.5	.3	.2	.5	.2
H ₂ + CO	11,485	14,580	12,480	14,660	11,280
Total carbon gasified	82.1	87.3	87.2	96.4	84.5
Coal required per M cu.ft. of (H ₂ +CO)	40.6	35.7	45.2	41.8	38.4
Oxygen required per M cu. ft. of (H ₂ +CO)	357	326	362	310	421
Process steam input required per M cu.ft. of (H ₂ +CO)	31.4	7.9	16.2	2.7	39.9
Carbon required per M cu. ft. of (H ₂ +CO)	28.6	25.0	27.7	24.2	31.6

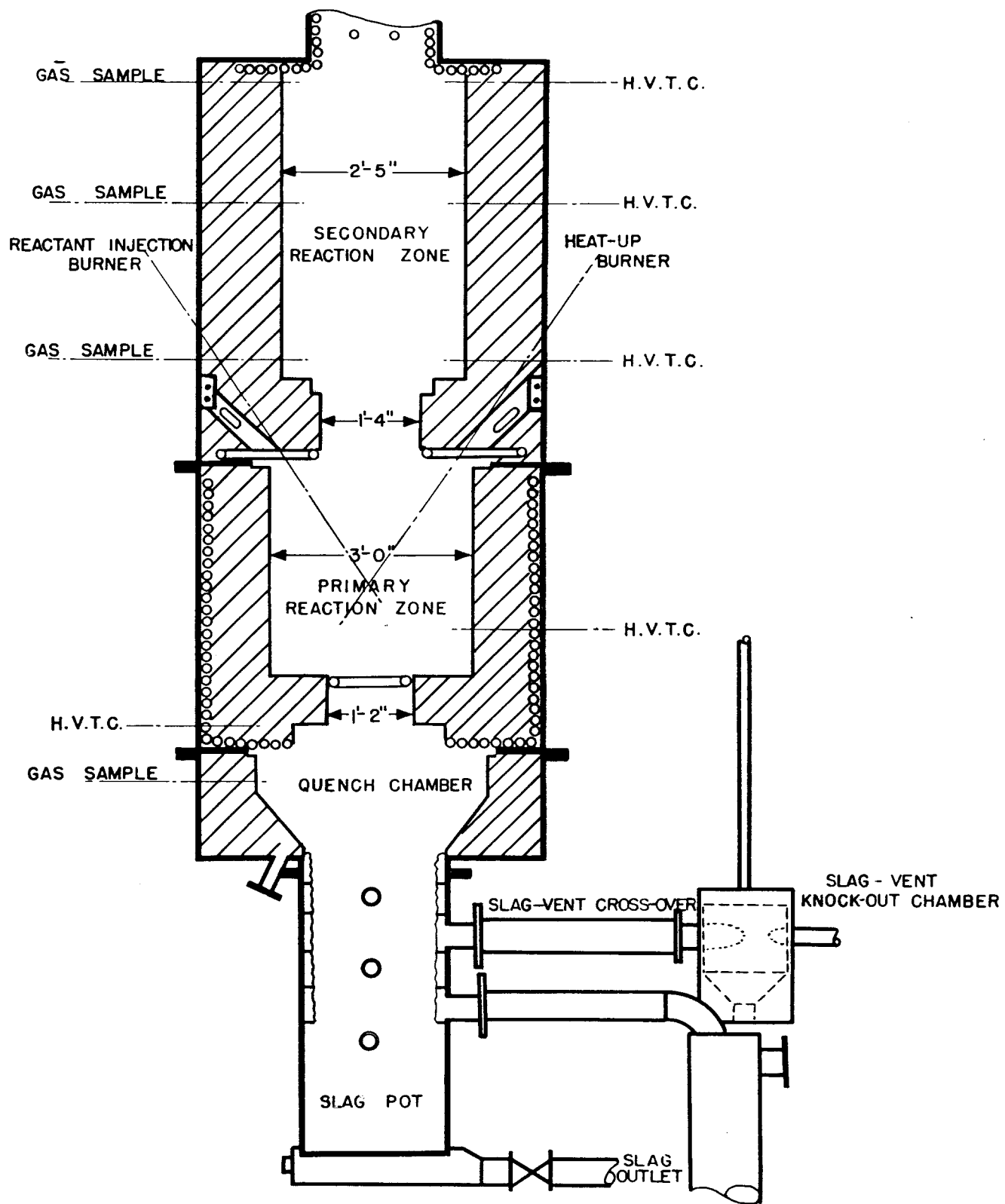


Figure 17. - Gasifier 4, design 5.

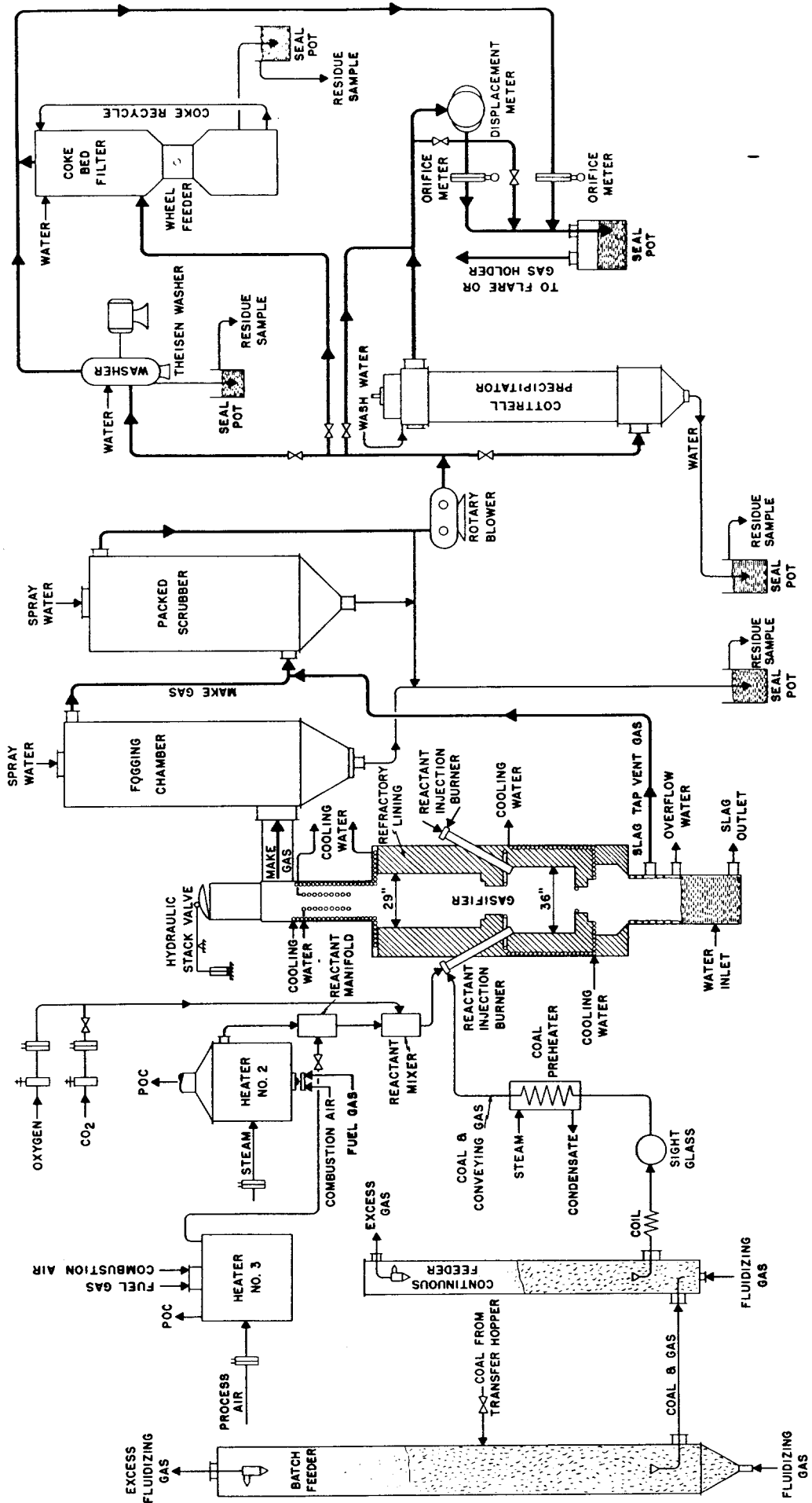


Figure 18. - Pilot-plant flowsheet for gasifier 4.

TABLE 3. - Properties of coals used in tests of atmospheric gasifier 4

Run No.....	34 Q	44	42 B	54 I	47 B
Type of coal	Sewickley, W. Va.	Roslyn, Wash.	Fries, Ky.	Lake de Smet, Wyom.	Anthracite, Pennsylvania
Proximate analysis, percent:					
Moisture	1.0	2.4	3.1	8.5	1.0
Volatile matter	34.6	37.7	35.4	41.3	7.0
Fixed carbon	49.6	47.3	43.4	39.0	81.9
Ash	14.8	12.6	18.1	11.2	10.1
Ultimate analysis, percent:					
Moisture	1.0	2.4	3.1	8.5	1.0
Ash	14.8	12.6	18.1	11.2	10.1
Hydrogen	4.8	5.2	3.7	4.4	2.8
Carbon	70.4	70.1	61.3	58.0	82.2
Sulfur	1.8	.4	3.4	.7	.6
Nitrogen	1.4	1.9	1.2	1.1	1.1
Oxygen	5.8	7.4	9.2	16.1	2.2
Calorific value.. B.t.u./lb.:					
Gross	12,618	12,720	10,995	9,970	13,550
Net	12,163	12,220	10,620	9,475	13,280
Ash fusibility.....°F.:					
Initial deformation	2,220	2,310	1,920	2,150	2,420
Softening	2,280	2,360	2,000	2,220	2,510
Fluid	2,390	2,526	2,310	2,380	2,570
Screen analysis, mesh:					
+50	Trace	0.0	Trace	0.3	0.0
-50 + 100	3.6	2.9	2.6	9.5	.4
-100 + 140	8.0	10.6	4.2	12.5	.6
-140 + 200	13.0	15.4	11.2	14.8	9.0
- 200	75.4	71.1	82.0	62.9	90.0

As a result of the development work, certain changes in the gasifier appeared desirable, and it is being modified as shown in figure 17. The important changes are: More adequate water cooling of the primary reaction zone to secure longer refractory life, and provision for additional temperature measurements and gas samples. Previously two types of refractory have been used in the lining of the gasifier. The Babcock & Wilcox Allmul, a high-alumina-content refractory, gave better results in the primary zone than the Babcock & Wilcox 80. The Babcock & Wilcox 80 lining, the only one used in the secondary zone, was in good condition after over 1,200 hours service. Samples of a silicon carbide refractory placed in the secondary zone showed no deterioration or slag penetration after over 1,200 hours service. In rebuilding the gasifier, a silicon carbide refractory, backed up by an insulating refractory, will be used in the primary zone and throat between the primary and secondary zones. In the secondary zone the Babcock & Wilcox 80 brick will be used again, backed by an insulating refractory.

A flowsheet for the process is given in figure 18. Minor changes have been made in the gas metering system to improve the accuracy of the data. Water scrubbing, followed by the use of a wet electrical precipitator, yields a gas clean enough

for synthesis use. Work is continuing on other methods for dust removal, including a moving-bed coke filter and a Theisen gas washer.

The reactant injection burners used in tests during 1953 are substantially of the same design as described in the 1952 Annual Report. The present design is efficient and good mixing of the reactants is obtained. However, it is necessary to introduce the steam-oxygen stream under some pressure, 40 to 60 p.s.i.g., to achieve good mixing, and it is believed that designs using lower pressures under 10 p.s.i.g. can be developed. Since burner design depends, in part, on the method used to feed the coal, an investigation to improve the design is being carried on, in concomitance with a study of feeding methods.

The recovery of heat from the product gas is advisable as a matter of economics. Regardless of the end use of this heat, it will undoubtedly be recovered in some type of waste-heat boiler with metal tubes. The top section of the gasifier was constructed to simulate such a boiler. Operation of the gasifier showed that deposits of ash or carbonaceous material on the tubing will present no serious difficulties. Using a variety of coals whose ashes have a wide range of fusion temperatures, deposits of such material could be removed with conventional soot-blowing equipment, even when the gas temperatures entering the cooling zone were within the plastic temperature range of the ash.

High-Pressure Gasifier

In processes requiring compressed synthesis gas, it is cheaper to gasify coal under pressure than to generate the gas at atmospheric pressure and subsequently compress it. Limitations imposed by the capacity of auxiliary equipment for the pressure gasifier at Morgantown did not permit complete determination of its capacity, that is, pounds of coal gasified per hour per cubic foot of reactor space, at various pressures, using the gasifier described in the 1952 Annual Report. Preliminary tests at a feed rate of 674 pounds per hour per cubic foot of reactor volume of Sewickley-bed coal showed approximately the same percentage of gasification, 90 percent, at 300, 200, and 100 pounds per square inch (see table 4). This indicates that the capacity of the gasifier is greater than 674 pounds per hour at 300 pounds per square inch.

The water-cooled refractories in the pressure gasifier were gradually eroded. Calculations showed that gasification could be carried out with reasonable consumption of coal and oxygen in a water-cooled reactor to which a thin layer of slag adhered, although the heat loss may be as high as 150,000 B.t.u. per square foot of reactor area. Owing to the high throughput obtained in the pressure gasification unit (over 600 pounds of coal gasified per cubic foot of reactor volume at 20 atmospheres) the heat loss even on this small reactor (11-inch tube, 3 feet long) would not be greater than about 1,000 B.t.u. per lb. of coal.

A cooling coil was designed and fabricated for installation in the reaction zone of the high pressure gasifier (see figs. 19 and 20). It consists of a helix wound from 1-1/4-inch schedule 80 pipe. The coil is 3 feet long and has an inside diameter of 12 inches. As originally installed, the inside diameter of the coil was studded with 3/4- by 3/8-inch studs of the type used in water-wall boilers. A 1-inch layer of chrome ore was spread over these studs, reducing the inside diameter of the reaction tube to 10 inches.

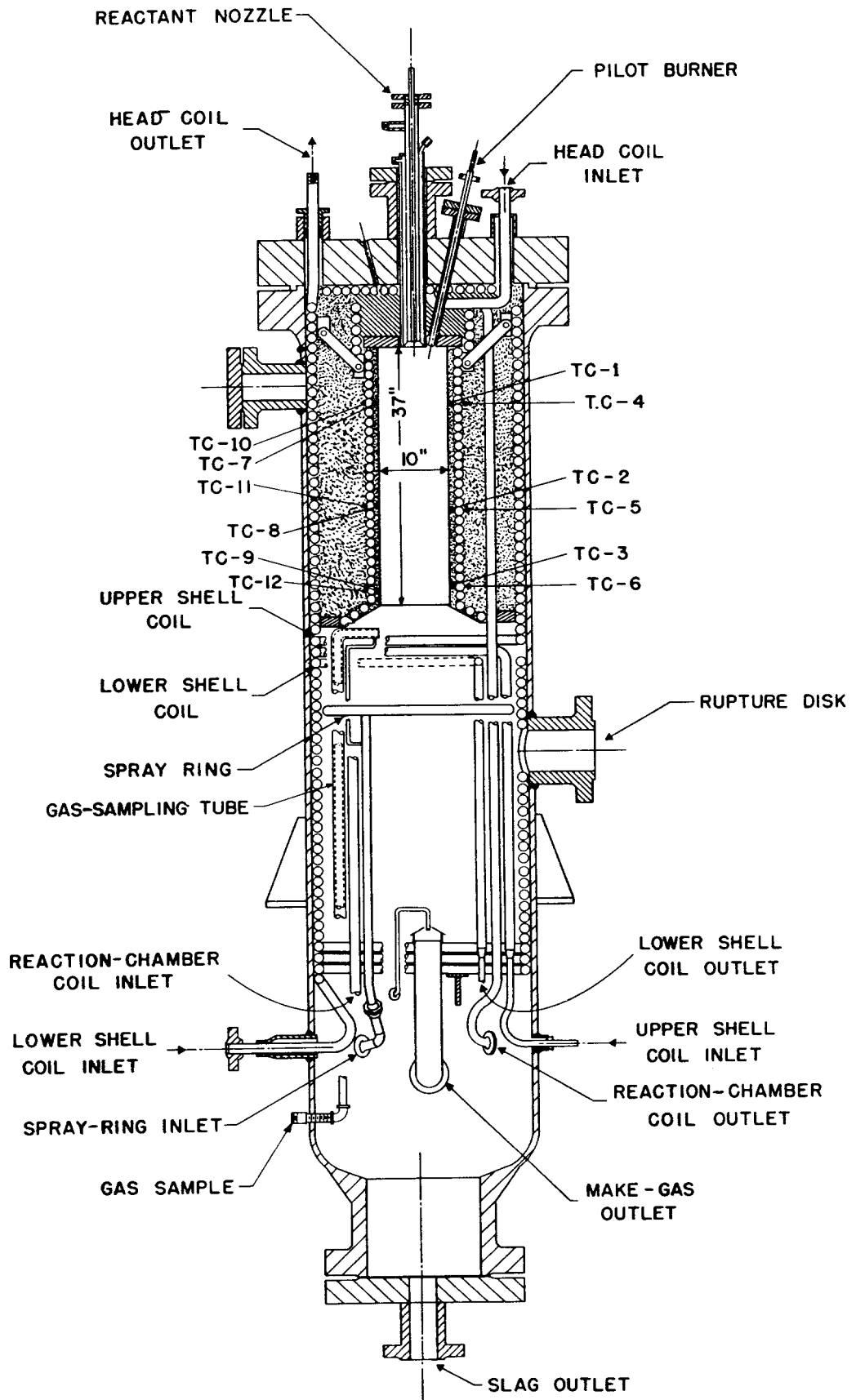


Figure 19. - Pressure gasifier 3.

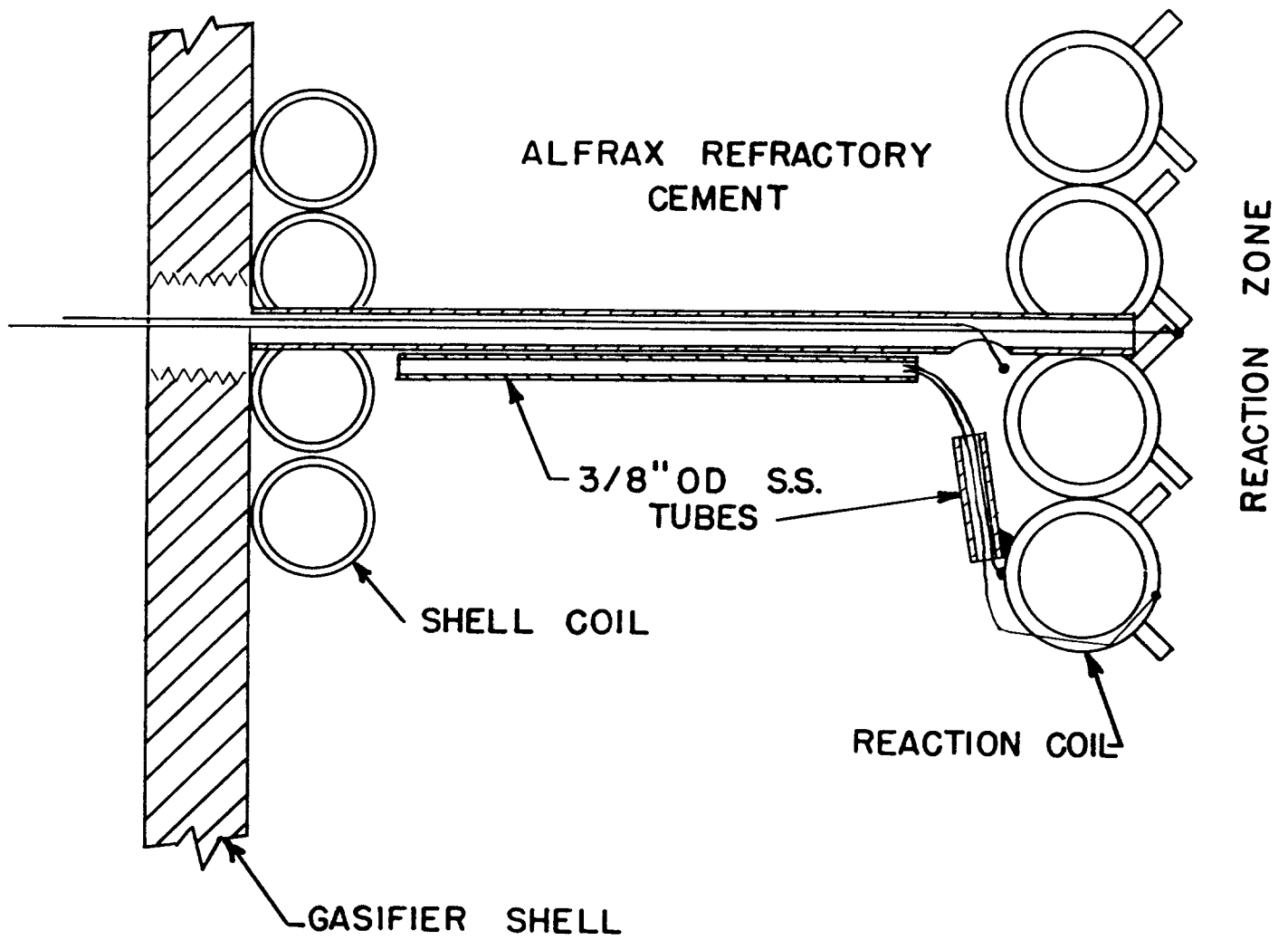


Figure 20. - High-pressure gasifier method of thermocouple installation at reaction coil.

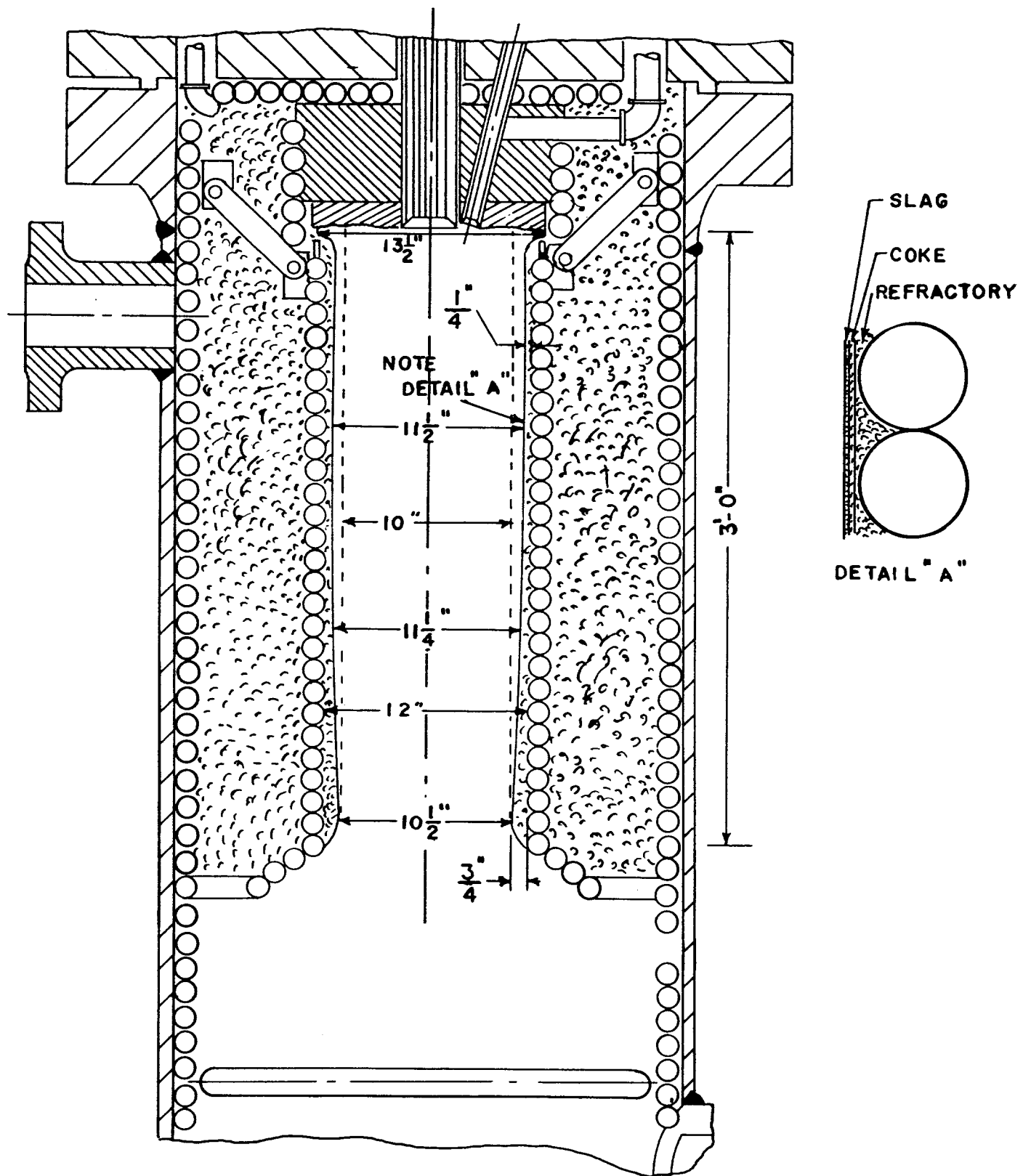


Figure 21. - Refractory condition of gasifier 3 following test P-39.

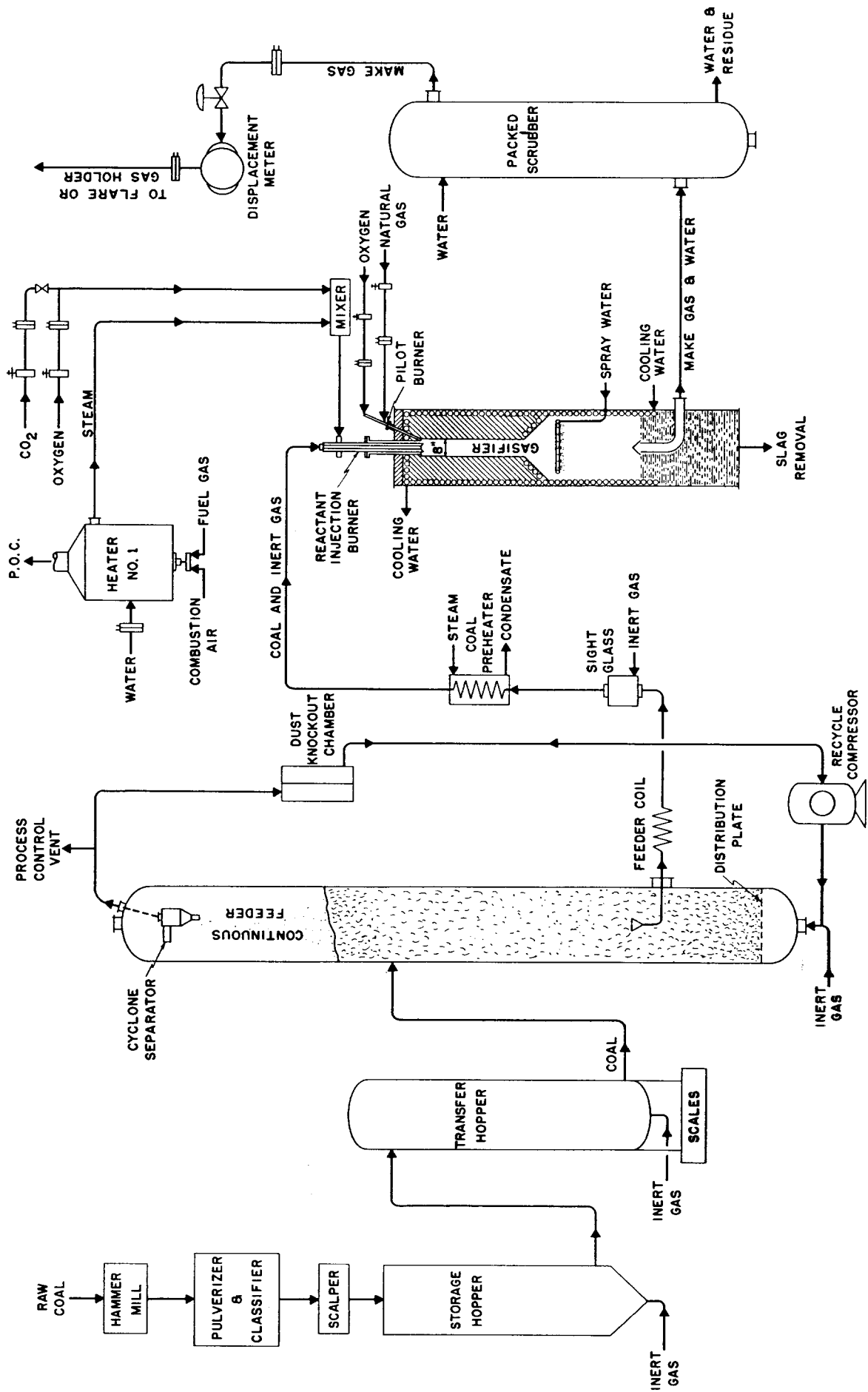


Figure 22. - Pilot-plant flowsheet for gasifier 3.

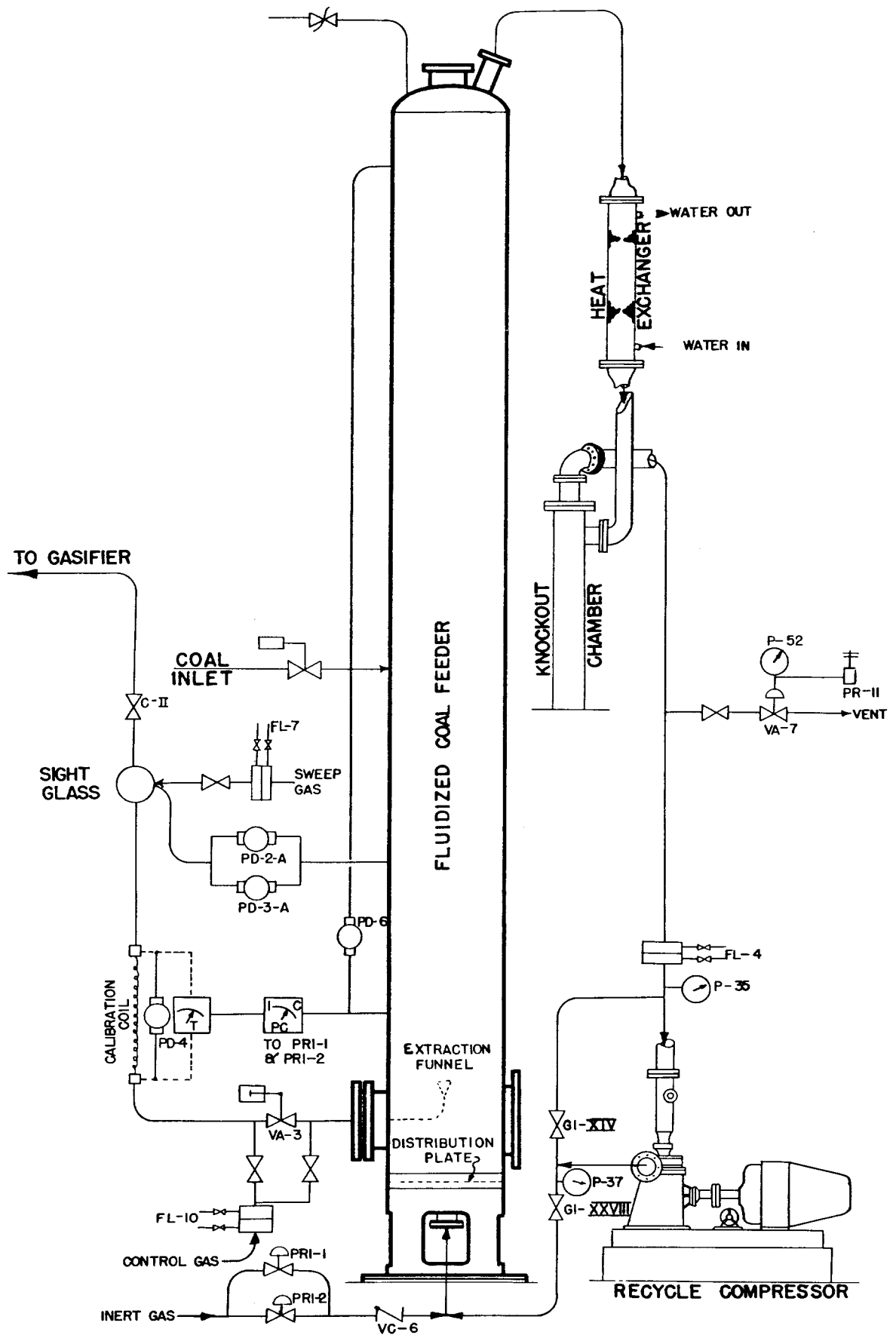


Figure 23. - Coal-feeder flowsheet for gasifier 3.