

Field-Scale Underground Gasification Experiments

The first field-scale underground gasification experiment was conducted at Gorgas, Ala., in 1947.<sup>96/</sup>

Preparations for the second field-scale experiment are in progress. In June 1948 the Federal Bureau of Mines and the Alabama Power Co. agreed to carry out the second underground gasification experiment, also at Gorgas, Ala., to obtain comprehensive data upon which to base plant-scale operations.

## LIQUEFACTION

A report covering Bureau of Mines research during the calendar year 1947 on the production of synthetic liquid fuels from both coal and oil shale was issued.<sup>97/</sup>

Production of Synthesis GasLaboratory-Scale Experimentation

A laboratory-scale pilot unit was designed and a method developed for the gasification of 10 to 30 pounds of pulverized bituminous coal per hour by entrainment in oxygen and steam at generator temperatures ranging from 1,800° to 2,400° F.

In the first series of runs, a noncoking bituminous coal, pulverized so that 72 percent passed through a 200-mesh screen, was charged at a uniform rate into the top of an 82-inch-long vertical refractory tube of 6 inches internal diameter. Engulfed in highly turbulent currents created by impinging oxygen and steam jets, the coal particles were gasified in entrainment, while the residual dust and fly ash were carried downward by the product gases, toward the outlet at the bottom. A self-explanatory flow diagram of the generator and purification train with wet handling of the products is shown in figure 33, and pictures of various parts of the unit and of the instrument board are shown in figures 34 and 35.

A series of runs made under widely different operating conditions proved that the quality of the synthesis gas made (percent combustible constituents, percent carbon dioxide content and carbon monoxide : hydrogen ratio) can be controlled by the proper choice of operating variables. However, the heat losses in internally heated generators of the size used are so excessive that considerably higher oxygen input was required per thousand cubic feet of synthesis gas made than for large plant-size units. The higher oxygen input resulted in a high ratio of carbon monoxide to hydrogen and much carbon dioxide in the make gas. Since an enormous amount of insulation would be needed to make the heat losses per cubic foot of generator volume equivalent to that in large-scale units, balancing of the heat losses by external heating of the generator chamber appears to be the logical way to approach operating conditions on large scale, which would allow the closest translation of the operating results for the designing of plant-size units.

Typical operating results from a 10-hour run, using the wet purification system are given in table 18.

<sup>96/</sup> Fies, Milton H., and Schroeder, W. C., Underground Gasification: Mech. Eng., vol. 70, No. 2, February 1948, pp. 127-135.

<sup>97/</sup> Report of the Secretary of the Interior on the Synthetic Liquid Fuels Act from January 1, 1947 to December 31, 1947 (to the 80th Cong.).

TABLE 18. - Operating results - run 13

Item	Period	Period	Period	Period	Total or weighted average of periods 1, 9, 10, 11
	1	9	10	11	
1 Duration of periods, hr. ....	0.73	1.00	1.00	1.58	4.31
2 Rate of coal feed, lb./hr. <sup>1/</sup> .....	9.79	9.79	9.79	9.79	9.79
3 Oxygen input, cu.ft./hr. <sup>2/</sup> .....	133	122	134	136	132
4 Total steam input, lb./hr. <sup>3/</sup> .....	2.55	2.21	2.61	3.53	2.84
5 Mol or volume ratio of oxygen to total steam .....	2.48	2.63	2.44	1.83	2.21
6 Steam input per lb. of coal, lb. ....	0.261	0.226	0.267	0.361	0.290
7 Output of gas, cu.ft./hr. <sup>2/</sup> .....	336	216	281	283	276
8 Cu. ft. oxygen input per MCF of gas ..	396	565	477	481	478
9 Coal feed in lb. per MCF of gas made <sup>2/</sup>	29.1	45.3	34.8	34.6	35.5
10 Combustible residue, lb./hr. <sup>4/</sup> .....					1.44
11 Percent carbon gasified in fuel charged (gasification efficiency) ..					78.5
12 Thermal efficiency (percent ratio of B.t.u. in gas to B.t.u. in coal) ...					57.4
13 Coal feed, lb. per MCF of CO + H <sub>2</sub> made <sup>1/</sup> .....	36.1	71.7	57.0	51.5	52.4
14 Cu. ft. oxygen input per MCF of CO + H <sub>2</sub> made .....	491	891	784	716	706
15 Lb. steam input per MCF of CO + H <sub>2</sub> made .....	9.41	16.13	15.26	18.58	15.19
16 Generator wall temperature, 8 inches from top, °F. ....	2,148	2,214	2,295	2,333	2,265
17 Generator wall temperature, 28 inches from top, °F. ....	1,897	1,684	1,761	1,823	1,789
18 Generator wall temperature, 59 inches from top, at bottom of silicon carbide tube, °F. ....	1,398	1,043	1,055	1,070	1,116
19 Generator wall temperature, 71 inches from top, °F. (slagging zone) .....	1,303	1,001	1,044	1,076	1,090
20 Gas analyses, percent: <sup>5/</sup>					
CO <sub>2</sub> .....	14.0	29.9	32.1	26.9	26.0
O <sub>2</sub> .....	1.4	1.8	1.0	1.5	1.4
Ill. (C <sub>2</sub> H <sub>4</sub> ) .....	.6	.5	.3	.3	.4
H <sub>2</sub> .....	44.0	26.6	25.8	27.6	30.4
CO .....	36.7	36.6	35.2	39.6	37.4
CH <sub>4</sub> .....	.3	1.4	2.6	2.8	2.0
N <sub>2</sub> .....	3.0	3.2	3.0	1.3	2.4
Calculated B.t.u. (60, 30, dry, gross) .....	274	227	229	251	246

<sup>1/</sup> On as-charged basis.<sup>2/</sup> Cu. ft. at 60° F., 30 in. Hg, dry, is shown in all cases.<sup>3/</sup> Includes steam from moisture in the coal charged, from water formed by the combination of oxygen with equivalent hydrogen in the coal, and from water vapors carried by the injected oxygen.<sup>4/</sup> On moisture- and ash-free basis.<sup>5/</sup> Corrected for CO<sub>2</sub> introduced for purging purposes.

The decomposition of methane in a porcelain tube at temperatures between 1,007° and 1,075° was studied.<sup>98/</sup> The following observations were made:

- (1) Within this range the first-order reaction constants increased with increasing decomposition.
- (2) There was a catalytic effect of acetylene, probably homogeneous, which accounts for (1), since the percentage of acetylene increased with increasing percentage of decomposition.
- (3) There was probably no effect of ethylene on the decomposition of methane.
- (4) There was a large catalytic effect of surface in the early stages of the reaction which disappeared by the time 30 percent of the methane was decomposed.
- (5) No induction period was found.
- (6) In the early stages of the decomposition, 50 percent nitrogen or steam in the entering gas resulted in about the same percentage of decomposition of the methane for equal contact time.

The production of alcohols is possible either as a primary objective or as an unavoidable by-product in the production of oil and gasoline by the Fischer-Tropsch process.<sup>99/</sup> Alcohols could serve as part of the motor fuel, and some of the higher molecular weight alcohols could command a relatively higher price and thus absorb part of the refining costs.

#### Purification of Synthesis Gas

For the production of synthetic liquid fuels it is proposed to produce synthesis gas directly from pulverized coal rather than from coke. For this reason purification problems are involved which are extremely difficult and unique so far as American gas-production practice is involved. The German<sup>100/</sup> synthetic-fuels industry avoided the production of synthesis gas from pulverized coal, partly because of anticipated purification difficulties, especially in connection with dust removal.

Impurities that may be present in gas made from pulverized coal and that must be removed include: Tar, dust, ammonia, hydrogen cyanide, naphthalene, gum-forming hydrocarbons, nitric oxide, hydrogen sulfide, and various organic sulfur compounds. Since removal of these impurities must be virtually complete, there are not only difficult purification problems to solve but also new requirements for sensitivity and precision in analytical methods used to determine the performance of purification processes.

Much progress has been made in the development of analytical methods. Previous methods have been improved to give greater precision and reduce the time required for obtaining analytical results.

<sup>98/</sup> Gordon, Alvin S., Pyrolysis of Methane Flowing Through a Porcelain Tube in the Region 1,000°: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 395-401.

<sup>99/</sup> Schroeder, W. C., Fischer-Tropsch Alcohol: Chem. Eng. Prog., vol. 44, No. 1, January 1948, pp. 15-17.

<sup>100/</sup> Sands, A. E., Wainwright, H. W., and Schmidt, L. D., The Purification of Synthesis Gas Produced from Pulverized Coal: Ind. Eng. Chem., vol. 40, April 1948, p. 607.

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#### Pilot-Plant-Scale Experimentation

Construction of the synthesis-gas pilot plant has progressed to the point where trial runs have been made in a Royster pebble stove. The generator has been completed and heated to about 2,000° F. Equipment for the automatic control of the process is being received and erected.

In addition to the work of erecting the pilot plant and making test runs on the stoves, research has been carried on with various refractory materials to determine their ability to withstand high temperatures (3,000° to 4,000° F.) and severe thermal shock. As a result of this work, several materials which appear to be satisfactory for pebble material and stove linings have been found.

The attached flow sheets (figs. 36 and 37) show the process; figures 38 and 39 are cross sections of the stoves and generator; and figure 40 is a close-up of the Royster Stoves and connections to the generator.

#### Demonstration-Plant Construction

The design of the 80- to 100-barrel-per-day Gas-Synthesis Demonstration Plant is well underway at Louisiana, Mo. Construction is in the grading and excavation stage. The plant will include pulverized-coal gasification with steam and oxygen, gas-purification, gas-synthesis, and product-distillation sections.

A 1-ton-per-hour capacity, 98 percent purity, Linde-Frankl oxygen plant was shipped from Hoechst, Germany, to Louisiana and was erected to provide the oxygen requirements for the gasification of pulverized coal.

#### Use of Oxygen in the Production of Synthesis Gas

The use of oxygen in the production of hydrogen or synthesis gas was reviewed.<sup>101/</sup> Processes for large-scale production of hydrogen and synthesis gas are basically identical. A plant producing 25,000 barrels of primary liquid fuel per day requires 700 to 800 million cubic feet of synthesis gas per day. Low-cost synthesis gas requires the use of lower-priced generator fuels, which can best be gasified in processes using oxygen. It was concluded that the American requirements may best be satisfied by gasifying pulverized fuel in suspension. This will permit the use of higher rank caking or noncaking coals, as well as lower rank subbituminous coals or lignite.

#### Synthesis of Liquid Fuels from Hydrogen and Carbon Monoxide

#### Laboratory-Scale Experimentation

Attention was called to the apparent impossibility of accounting for the isomeric composition of Fischer-Tropsch hydrocarbons on the basis of the carbidic carbon-methylene polymerization hypothesis.<sup>102/</sup> The hydrocarbon product, boiling in the gasoline range, has been found to contain 10 to 15 percent of singly branched hydrocarbons

<sup>101/</sup> Newman, L. L., Oxygen in the Production of Hydrogen or Synthesis Gas: Ind. Eng. Chem., vol. 40, April 1948, pp. 559-582.

<sup>102/</sup> Storch, H. H., Review of Development of Processes for Synthesis of Liquid by Hydrogenation of Carbon Monoxide: Chem. Eng. Progress, vol. 44, 1948, No. 6, pp. 469-480.

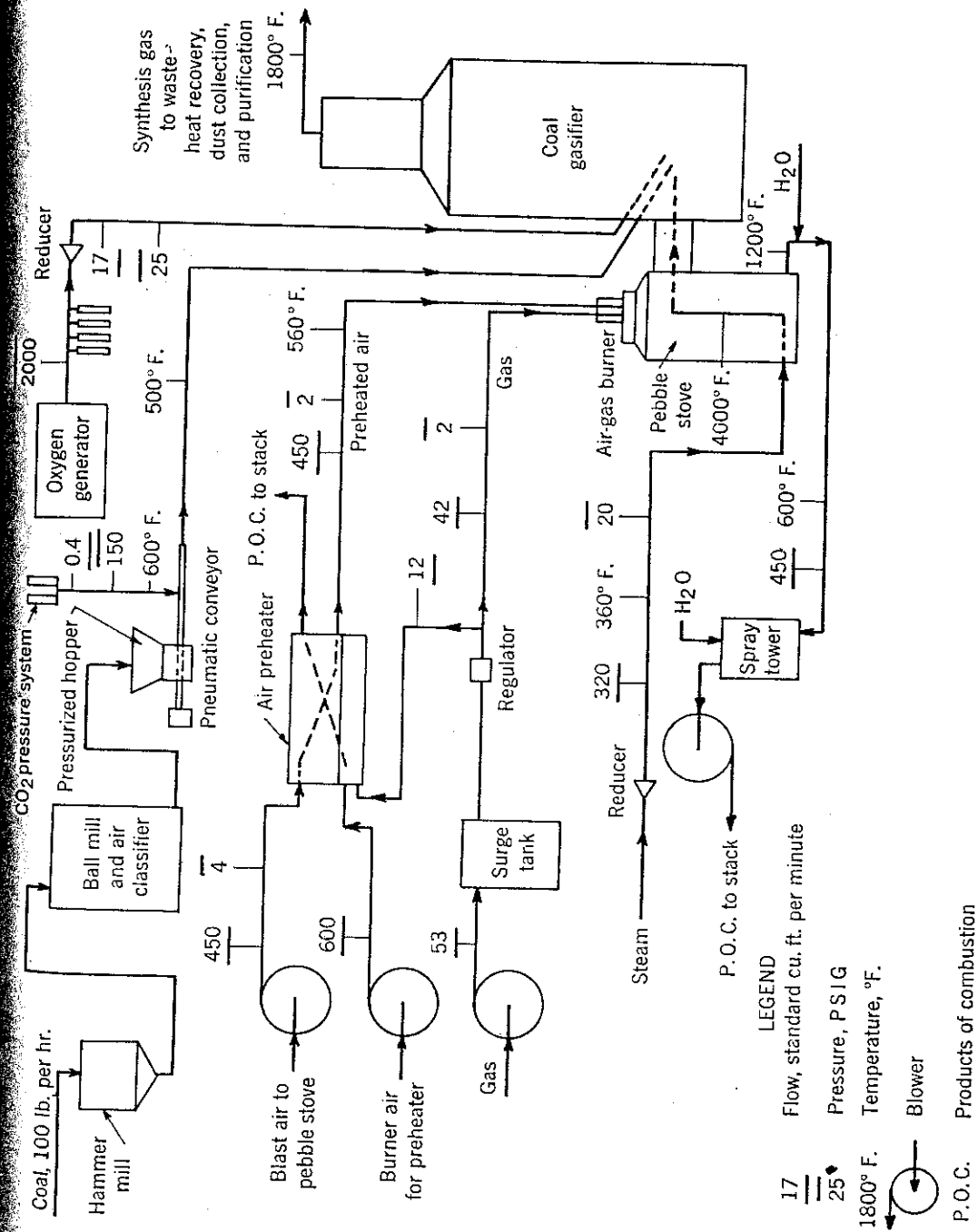


Figure 36. - Flow sheet for plant gasifying pulverized coal.

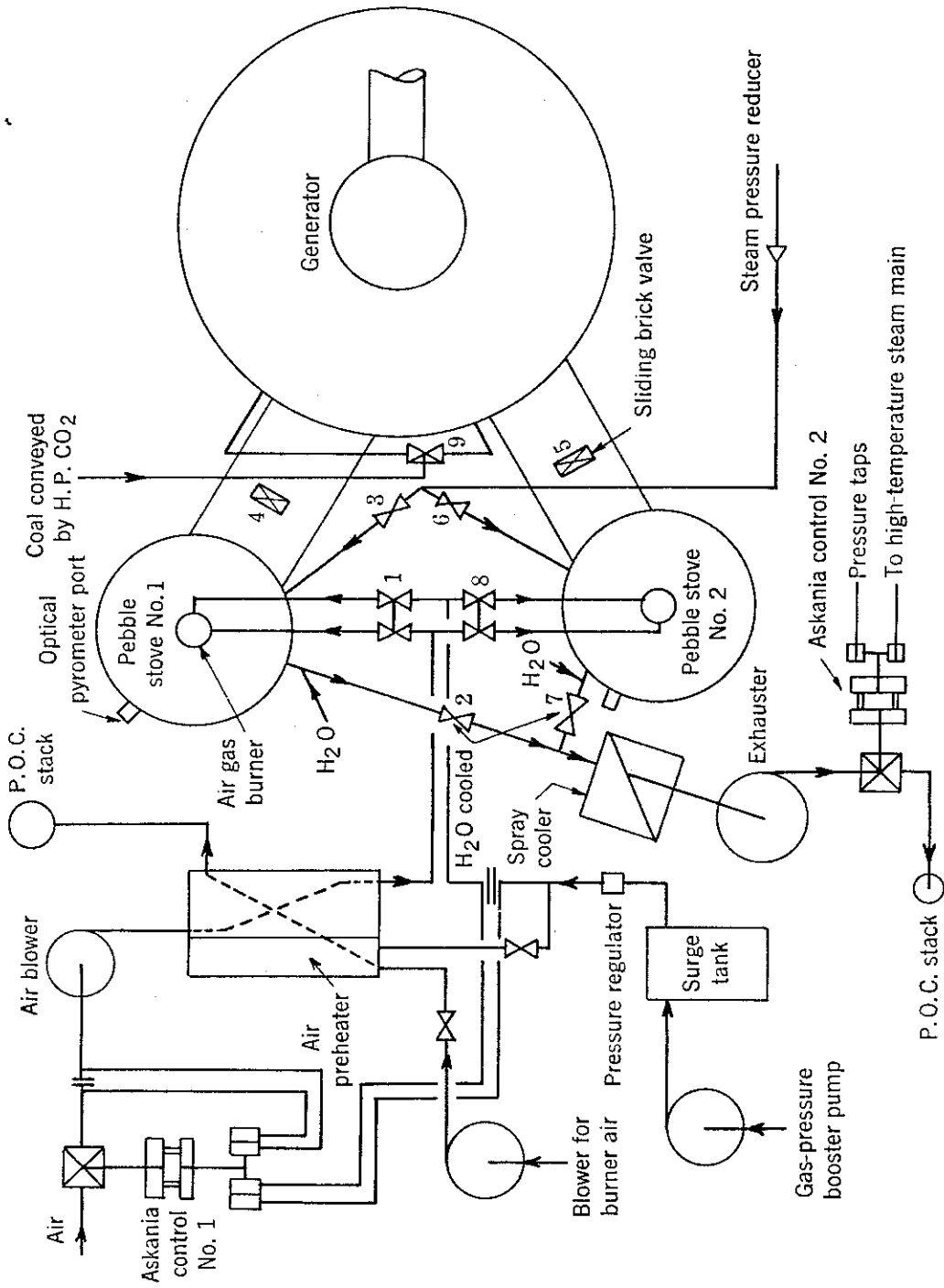


Figure 37. - Valve and Instrumentation diagram.

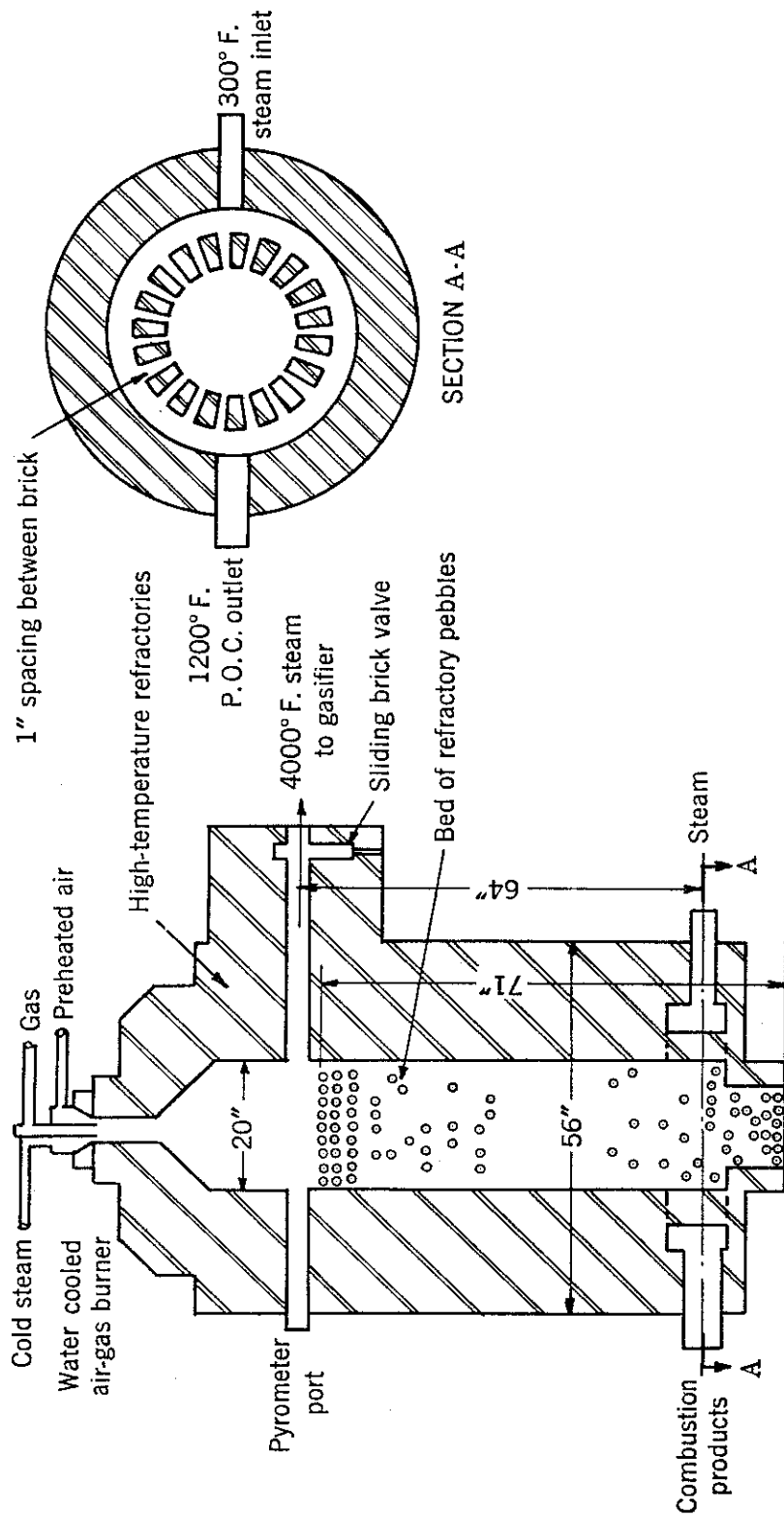


Figure 38. - Royster pebble stove to superheat reaction steam in pulverized-coal-gasification plant.

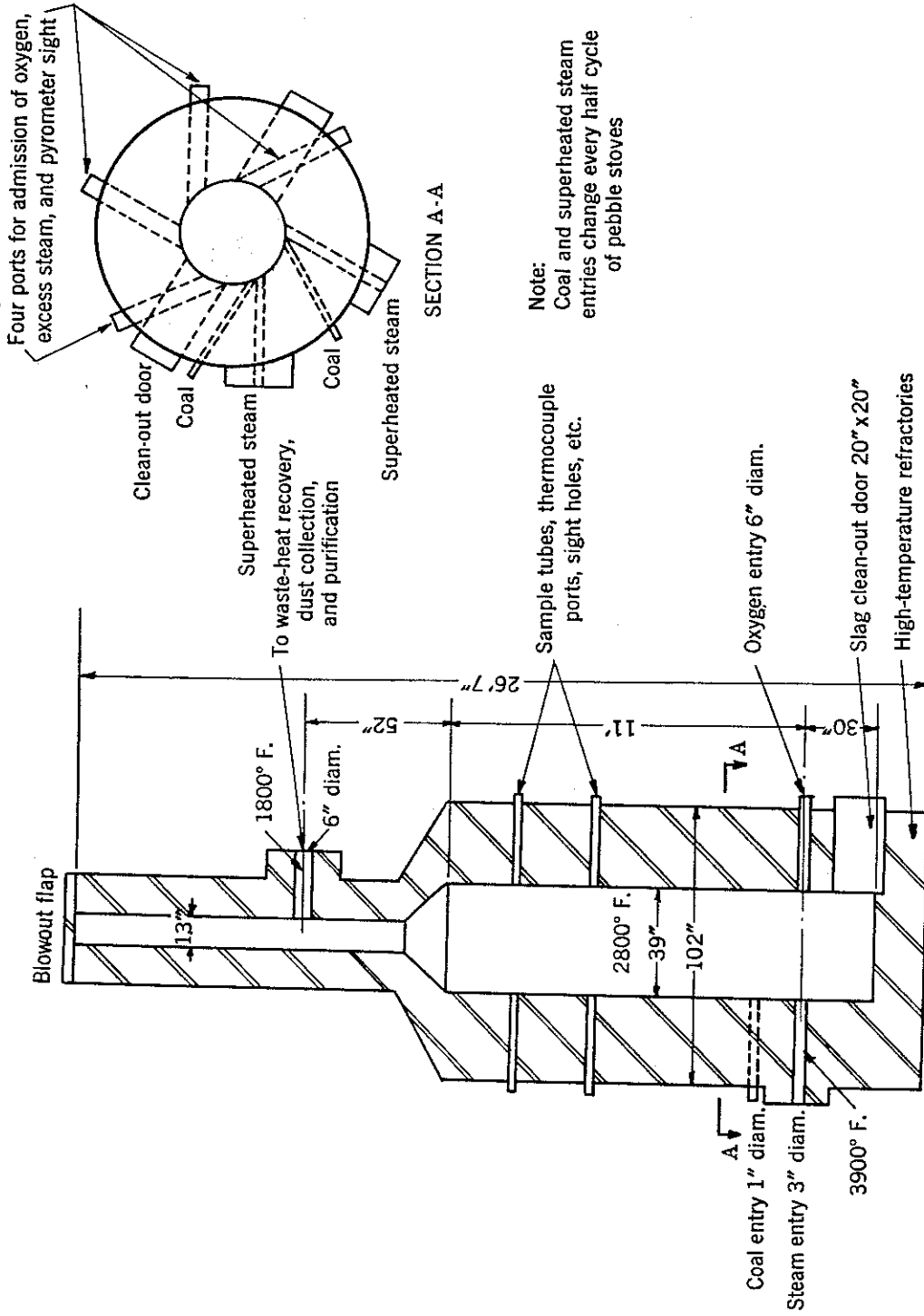


Figure 39. - Coal gasifier for coal-gasification plant.



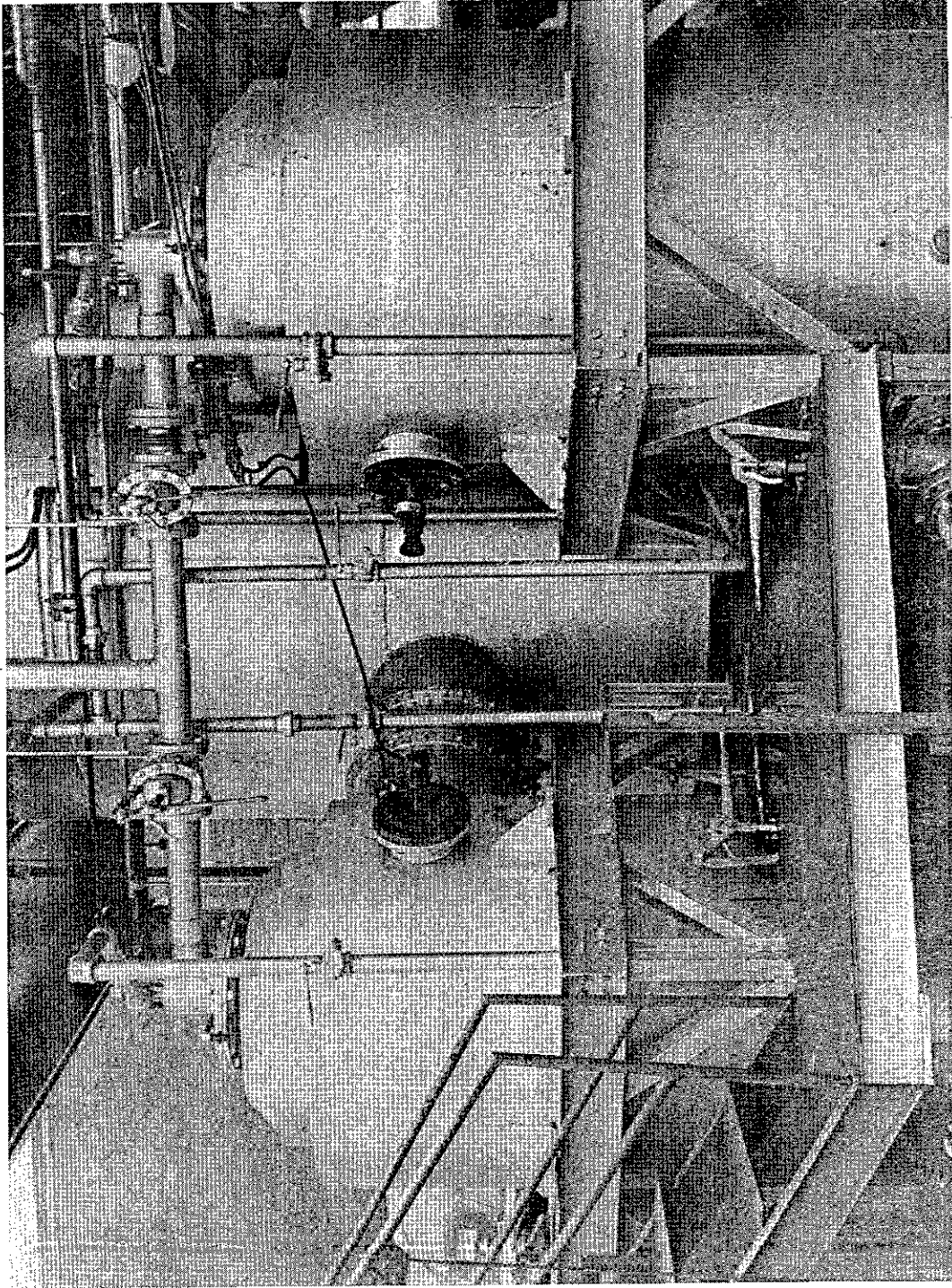


Figure 40. - Close-up view of Royster stoves and connections to the generator.

with a methyl group in the 2 or 3 position. No appreciable amounts of multiple-branched hydrocarbons or of branches containing more than one carbon atom have been found. If the mechanism of the synthesis involves carbidic carbon and methylene group polymerization, branching would occur whenever a carbidic carbon is added to the chain of methylene groups. According to this mechanism, there is no obvious limitation to the number of branches per molecule or to the length of a branch.

Another fact that is extremely difficult to explain on the basis of the carbidic carbon-methylene polymerization mechanism is that alcohols are the precursors of olefins in the "synol" process. The latter is identical with the Fischer-Tropsch synthesis on iron catalysts, except that a much higher degree of recycling of end gases with removal of carbon dioxide in each cycle is employed. The product of the synol process contains 50 to 60 percent of chiefly normal alcohols, as compared with 20 to 30 percent in the product of the Fischer-Tropsch process. Because the essential difference between the synol and the Fischer-Tropsch synthesis is the much shorter retention time of the products in the former process, it is probable that normal alcohols are early products and that the olefins result from dehydration of these alcohols.

In an attempt to explain the facts concerning the composition of Fischer-Tropsch products, it was suggested that a reaction similar to the "OXO" reaction may occur on the surface of catalysts during the synthesis of hydrocarbons and alcohols by the Fischer-Tropsch and synol processes. The essential features of the "OXO" process have been reviewed and a mechanism for the reaction proposed.<sup>103/</sup> This process consists in reacting olefins with carbon monoxide and hydrogen to produce aldehydes and subsequent reduction of the latter with hydrogen to alcohols. The basic reaction was discovered by the Ruhrchemie, and a large-scale continuous process resulted from cooperative efforts of Ruhrchemie and I. G. Farbenindustrie. A slurry of liquid olefin plus 3 to 5 percent reduced Fischer-Tropsch cobalt-thoria-magnesia-kieselguhr catalyst is pumped along with 1 H<sub>2</sub> + 1 CO gas (about 0.2 cubic meter per liter of olefins) through a preheater (150-160° C.) into two reactors at 200 atmospheres pressure. The second reactor is in series with the first, and an equal amount of gas (0.2 cubic meter per liter of olefin) is pumped into the second reactor. The excess H<sub>2</sub> + CO in both reactors serves to agitate the reaction mixture. Ethylene and propylene react readily when used in solution in a liquid medium. The contact time is about 20 minutes. Most of the catalyst is filtered off and recycled. The conversion is 70 percent in the first reactor and 30 percent in the second. The product consists of 80 percent aldehydes (about one-fourth of this is polymerized aldehyde) and 20 percent alcohols. It is not practical to isolate aldehydes from the first stage and it is considered preferable to dehydrogenate the corresponding alcohols from the second stage.

Because hydrogenation of the aldehydes is retarded by carbon monoxide, the first-stage product must be let down to atmospheric pressure. The second stage is operated with hydrogen at 170°-195° C. and at 200 atmospheres pressure. Fischer-Tropsch cobalt catalyst (from the first stage) or copper chromite may be used in the second stage. If the former is used, some carbon monoxide is formed by decomposition of cobalt carbonyl, and the exit gas is passed over an iron catalyst at 250° C. to convert the carbon monoxide to methane, whose concentration up to about 10 percent is of only slight importance. The second stage is otherwise identical with the

<sup>103/</sup> Wender, I., and Orchin, M., Critical Review of Chemistry of OXO Synthesis for Production of Alcohols from Olefins, Carbon Monoxide and Hydrogen, with Discussion of Reaction Mechanism for OXO and Related Syntheses: Bureau of Mines Rept. of Investigations 4270, 1948, 26 pp.

first. The first stage is not affected by sulfur compounds, but the second is very sensitive; and, if sulfur compounds are present, sulfide catalysts (such as mixture of nickel and tungsten sulfides) must be used.

The reaction in the first stage probably is a homogeneous catalytic reaction with either cobalt carbonyl or cobalt hydrocarbonyl as the catalyst. The insensitivity to sulfur poisoning and the fact that any finely divided reactive cobalt compound may be used support this assumption.

The aldehydes and alcohols produced are a mixture of normal and isocompounds. This is due not only to orientation of the hydrogen with respect to the carbon-carbon monoxide bonds in the initial reaction complex, but also to isomerization of the olefin under the process conditions. It may be significant that nickel carbonyl does not readily shift the olefin double bond under the OXO-process conditions, and nickel compounds are very poor catalysts for the process. From isooctene, 32 percent of n-nonyl alcohol and from propylene 50 percent of n-butyl alcohol are obtained, the remainder of the products being iso-alcohols. In general, using x-olefins as raw material one obtains about 60 percent of isocalcohols. The synthesis will not occur unless a labile hydrogen atom is available in the olefin reactant; with diolefins, the reaction takes place at only one double bond.

This suggestion<sup>104/</sup> leads to the assumptions that the chief reactions occurring on a Fischer-Tropsch catalyst are:

- (1) Formation of methylene groups by reduction of chemisorbed carbon monoxide.
- (2) Formation of ethanol by addition of carbon monoxide and hydrogen to a methylene group.
- (3) Dehydration of ethanol to ethylene.
- (4) Steps similar to 2 and 3, starting with ethylene, propylene, etc., for formation of higher alcohols and olefins.

In this series of reactions, alcohols are the precursors of the olefins; not more than one branch per molecule can be formed; and, because of steric factors, formation of branches containing more than one carbon atom is highly improbable.

From a bed of cobalt-thoria-kieselguhr catalyst 36 inches deep contained in a 1/2-inch-diameter laboratory converter,<sup>105/</sup> samples were removed at points 2-1/2 inches apart. Five percent argon was added to the original synthesis gas as an inert reference component. The rate of removal of a sample was slow enough so as not to cause any appreciable perturbation in the total flow of synthesis gas through the reactor.

The synthesis rate was high in the initial part of the bed, and lower and fairly constant throughout most of the catalyst bed, until the reactants were virtually completely consumed. Over the range of constant synthesis rate, the gas composition

<sup>104/</sup> See footnote 103, p. 77.

<sup>105/</sup> Anderson, R. B., Krieg, A., Seligman, B., and O'Neill, W. E., Studies of the Fischer-Tropsch Synthesis. Part I. Tests with Cobalt Catalysts at Atmospheric Pressure: Ind. Eng. Chem., vol. 39, 1947, pp. 1548-1554.

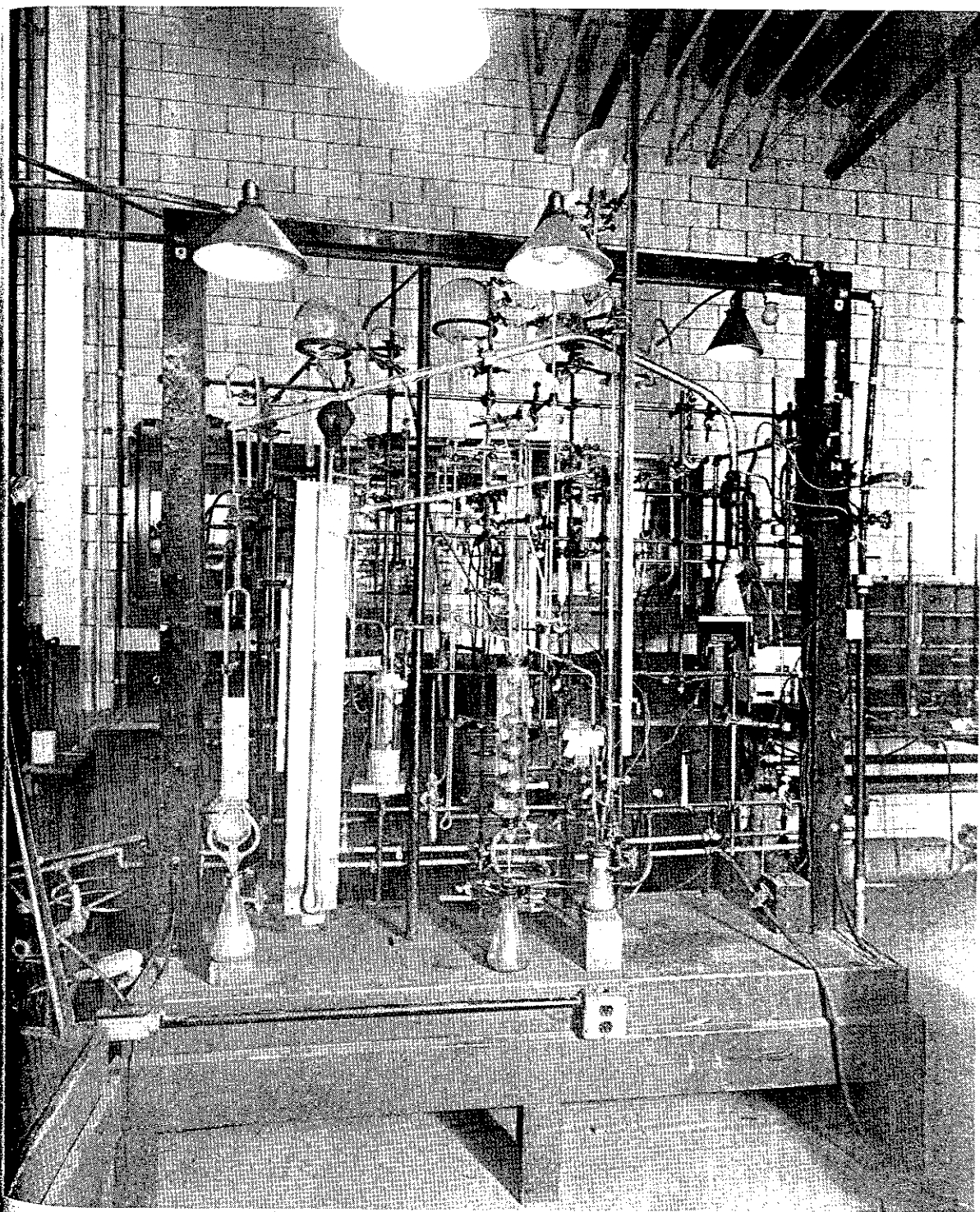


Figure 41. - Apparatus for measuring surface areas of catalysts.



varied considerably. Methane and carbon dioxide were formed by primary reactions; methane also was formed by secondary hydrocracking of higher molecular weight hydrocarbons, and carbon dioxide by the water-gas shift reaction. These reactions occurred throughout the catalyst bed, and their extent depended upon the composition of the gas in contact with the catalyst.

The X-ray diffraction patterns of cobalt carbide<sup>106/</sup> and of the three iron carbides<sup>107/</sup> have been accurately determined. This information combined with the magneto-chemical constants<sup>108/</sup> and earlier determinations of such patterns and constants for the iron oxide phases<sup>109/</sup> have provided the essential elements for analysis of Fischer-Tropsch catalysts by physical methods. An interesting byproduct of the work on the physical properties of the various iron oxides was the determination of the nature of iron compounds in red and yellow sandstone.<sup>110/</sup>

Measurements,<sup>111, 112/</sup> of pore volumes, and activated adsorption of carbon monoxide are being made on all catalysts tested. For iron catalysts which are fused or highly sintered, the desirability of complete reduction with hydrogen prior to use in the synthesis is best explained by the creation of a system of pores and fissures by the reduction.

A photograph of apparatus used for surface area measurements is shown in figure 41.

To insure reproducibility of pilot plant operations, all catalyst preparations are tested for their activity, and some indications of durability are obtained during several weeks of operations in catalyst testing units. A large proportion of catalyst testing involves the search for cheaper iron catalysts of suitable mechanical form, activity, and durability. The most promising catalyst for the internally cooled process consists of magnetite-ore fines which have been impregnated with alkali and copper solutions, extruded, dried, and sintered. For the slurry process, special precipitated-iron catalysts and those prepared by ignition of ferric nitrate-starch mixtures have been most promising.

<sup>106/</sup> Hofer, L. J. E., and Peebles, W. C., X-ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2497-2500.

<sup>107/</sup> Weller, S., Kinetics of Carbiding and Hydrocarbon Synthesis with Cobalt Fischer-Tropsch Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 2432-2436.

<sup>108/</sup> Weller, S., Hofer, L. J. E., and Anderson, R. B., The Role of Bulk Cobalt Carbide in the Fischer-Tropsch Synthesis: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 799-801.

<sup>109/</sup> Storch, H. H., Hawk, C. O., Golumbic, N. R., Hofer, L. J. E., and Anderson, R. B., Synthetic Liquid Fuel Processes. Hydrogenation of Carbon Monoxide, Part I. Review of Literature and Data on Effect of Preparation, Reduction, and Induction Procedures on Catalyst Activity; and on Correlation of Activity with Physical Properties of Catalysts: Bureau of Mines Tech. Paper 709, 1948, 213 pp.

<sup>110/</sup> Hofer, L. J. E., and Weller, S., The Nature of the Iron Compounds in Red and Yellow Sandstone: Science, vol. 107, 1947, p. 470.

<sup>111/</sup> Anderson, R. B., Hall, W. K., Hewlett, H., and Seligman, B., Studies of the Fischer-Tropsch Synthesis II. Properties of Unreduced Catalysts: Jour. Am. Chem. Soc., vol. 69, 1947, pp. 3114-3119.

<sup>112/</sup> Anderson, R. B., and Hall, W. K., Modifications of the Brunauer, Emmett, and Teller Equation I: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 1727-1734.

A sample of Ruhrchemie catalyst 234, containing iron, copper, calcium oxide, potassium oxide, and diatomaceous earth in the proportions by weight of 100 : 2.5 : 10 : 3 : 15 and several batches of Bureau of Mines iron-copper-potassium oxide - 100 : 10 : 0.5, were tested. Both catalysts were prepared by precipitation from aqueous solutions of the nitrates of iron and copper. For these catalysts, reduction with hydrogen was found to be undesirable, compared with an induction with either  $2H_2 + 100$  gas at  $255^\circ C.$ , or with  $1H_2 + 100$  at  $230^\circ C.$ , at atmospheric pressure before use in the synthesis at 7 atmospheres pressure. The yield obtained at  $230^\circ C.$  and 7 atmospheres was 125 grams of hydrocarbons from propane to wax, per cubic meter of synthesis gas. Of this yield, about 100 grams per cubic meter were hydrocarbons from pentane to wax. This yield decreased during 12 weeks of operation by about 20 percent.

A photograph of the rebuilt catalyst testing units is shown in figure 42.

A correlation was developed<sup>113/</sup> which permits the estimation of heat transfer coefficients if the physical properties of the fluid and the dimensions of the apparatus are known. A maximum heat transfer coefficient was noted with the ratio of particle to tube diameter was about 0.15. The effects of uniformity of packing, shape, surface roughness, and thermal conductivity of the granules were studied. The results showed a negligible effect of surface roughness, and a definite relationship between thermal conductivity and heat transfer rates.

This research<sup>114, 115, 116, 117, 118, 119/</sup> was done to make possible more accurate estimates of the energy requirements of the Fischer-Tropsch hot-gas recycle and other processes in which large linear velocities of gases through packed tubes were necessary. A general relationship was developed from experimental data on pressure drop through packed tubes which quantitatively correlates the shape and roughness of the granules and the packing density with the pressure drop. Graphic methods for estimating the percentage of voids from the size and shape of the granules and the dimensions of the vessel were developed.

Work on the liquid-phase catalyst suspension process using a laboratory-size reactor yielded valuable data on the effects of catalyst concentration, gas flow rate, temperature, and pressure. Because these tests indicated a much lower durability of the catalysts than was expected from data in captured German documents, a careful study was made of the effects of the degree of uniformity of the catalyst suspension and of the linear velocity of gas and liquid flows, as well as of particle size of catalyst. Using these data, a pilot plant of 1 to 3 gallons per day capacity has been designed and operated.

<sup>113/</sup> Leva, M., Heat Transfer to Gases Through Packed Tubes: Ind. Eng. Chem., vol. 39, 1947, pp. 857-859.

<sup>114/</sup> Leva, M., Pressure Drop Through Packed Tubes, Part I. A General Correlation: Chem. Eng. Progress, vol. 43, 1947, pp. 549-554.

<sup>115/</sup> Leva, M., and Grummer, M., Pressure Drop Through Packed Tubes, Part II. Effect of Surface Roughness: Chem. Eng. Progress, vol. 43, 1947, pp. 633-638.

<sup>116/</sup> Leva, M., and Grummer, M., Pressure Drop Through Packed Tubes, Part III. Prediction of Voids in Packed Tubes: Chem. Eng. Progress, vol. 43, 1947, pp. 713-718.

<sup>117/</sup> Brinkley, S. R., Contact Times of Continuous-Flow Reaction Systems with Volume Change: Ind. Eng. Chem., vol. 40, 1948, pp. 303-307.

<sup>118/</sup> Leva, M., and Grummer, M., Heat Transfer to Gases Flowing in Turbulent Motion Through Packed Tubes: Ind. Eng. Chem., vol. 40, 1948, pp. 415-419.

<sup>119/</sup> Leva, M., Weintraub, M., Grummer, M., and Clark, E. L., Cooling of Gases Through Packed Tubes: Ind. Eng. Chem., vol. 40, 1948, pp. 747-752.

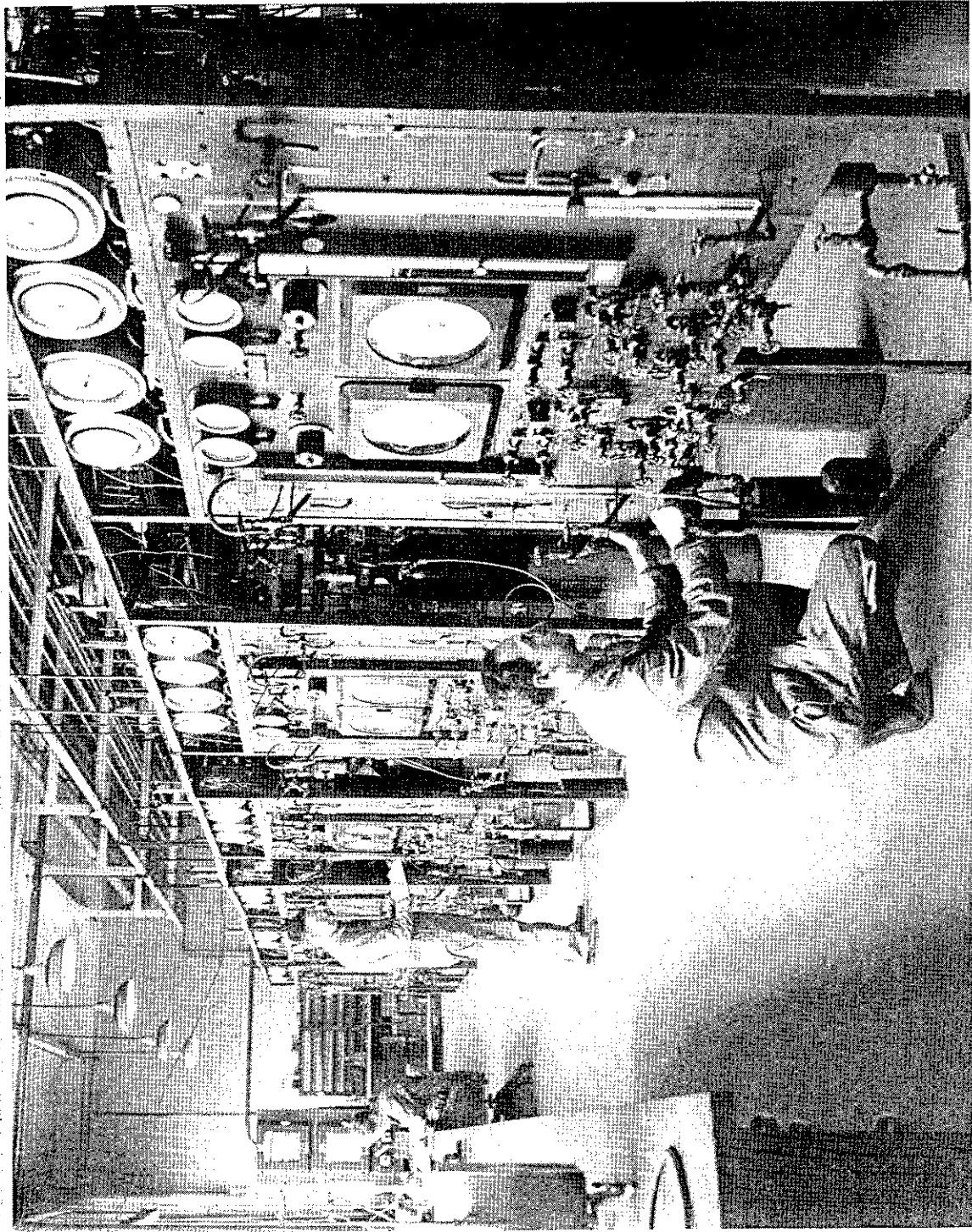


Figure 42. - Catalyst testing units.

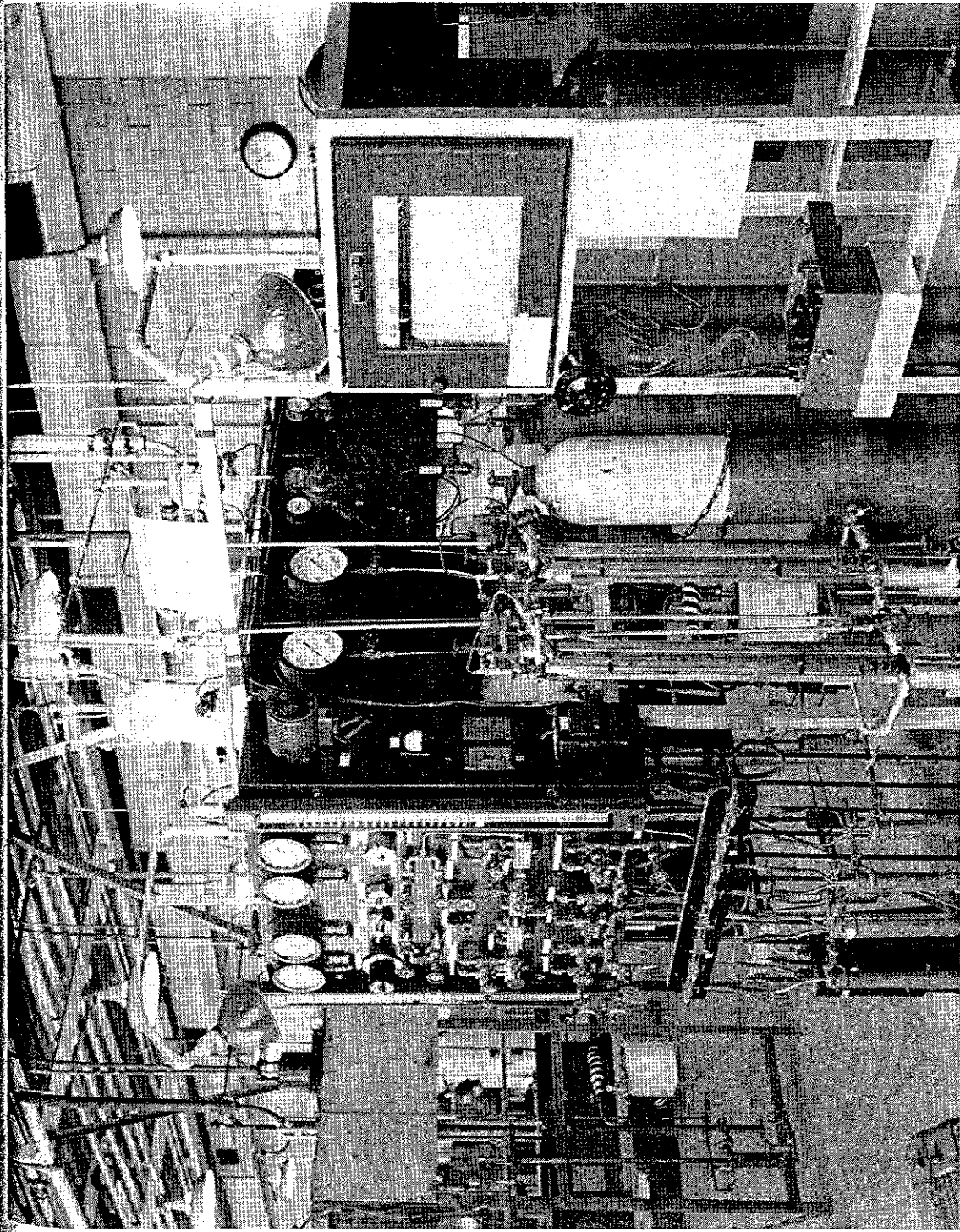


Figure 43. - Equipment for study of effect of reduction conditions on iron-catalyst activity.



A detailed study was made of the effects of different degrees of reduction of fused synthetic ammonia-type iron catalyst, using the apparatus shown in figure 43. For maximum durability and activity, virtually complete reduction is desirable. The rate of reduction at any given temperature is greatly reduced by small amounts of water vapor and by carbon monoxide and carbon dioxide impurities in the hydrogen.

The isomeric composition of Fischer-Tropsch hydrocarbons boiling in the gasoline range (up to 200° C.) is being carefully measured, using the infrared and the mass spectrometers. Because the bulk of the fractions consists of normal straight-chain hydrocarbons, appreciably better resolution is obtained with the mass spectrometer. Products from cobalt and iron catalysts and from different iron-catalyst processes are being analyzed. The results thus far show that, for both cobalt and iron catalyst products, 10 to 25 percent of singly branched hydrocarbons is present. The branching is usually at the 2- or 3-carbon-atom position. No branch larger than a methyl group and no multiple-branched molecules have been found.

Infrared analyses of fractions of the paraffin-naphthene fractions of light oil from coal hydrogenation have confirmed older analyses based on boiling range, refractive index, etc.

A fairly complete quantitative analysis has been made of the phenol, cresol, and xylenol fractions of tar acids in coal-hydrogenation oils. Starting with a large sample of hexane-soluble oil, the tar acids were extracted with alcoholic caustic. The tar acids were separated after acidification of the extract. After evaporation of the solvent, the crude phenols constituted 9.6 percent of the hexane-soluble oil. 63.5 percent of the crude phenol was distillable below 180° C. at 2.5 mm. of mercury pressure. The distillable tar acids were fractionally distilled and the phenol, cresol, and xylenol fractions separated. The constituents of these fractions were qualitatively identified by preparation of derivatives of known physical properties, and quantitatively determined by infrared spectrometry. Infrared techniques were improved by studies of radiation sources<sup>120/</sup> and of calibration methods.<sup>121/</sup>

In addition to infrared analysis, another quantitative procedure for separation and determination of individual tar acids is being studied. This procedure involves countercurrent distribution between immiscible solvents. The differences in partition coefficients in the system cyclohexane - 0.5 m. phosphate aqueous solution of pH 11.08 are large enough to permit such quantitative separations. Standardization tests are being made, and it is expected that this procedure will make it possible to effect separations which cannot be made by any other method.

The isolation and identification of polynuclear hydrocarbons<sup>122/</sup> in coal hydrogenation oils is being greatly aided by precise ultraviolet spectrometric measurements.<sup>123/</sup>

<sup>120/</sup> Friedel, R. A., and Sharkey, A. G., Jr., Comparison of Glowler and Globar Sources for Infrared Spectrometry: Rev. Sci. Instr., vol. 19, 1947, pp. 928-930.

<sup>121/</sup> McKinney, D. S., and Friedel, R. A., Calibration Method for Infrared Prism Spectrometers: Jour. Opt. Soc. America, vol. 38, 1948, pp. 222-225.

<sup>122/</sup> Woolfolk, E. O., Orchin, M., and Storch, E. H., Note on the Constitution of Heavy Oil from Coal Hydrogenation: Fuel in Sci. & Prac., vol. 26, May-June 1947, p. 78.

<sup>123/</sup> Friedel, R. A., Orchin, M., and Reggel, L., Steric Hindrance and Short Wave-length Bands in the Ultraviolet Spectra of Some Naphthalene and Diphenyl Derivatives: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 199-204.