RESEARCH AND DEVELOPMENT, COAL-TO-OIL LABORATORIES AND PILOT PLANTS, BRUCETON AND PITTSBURGH, PA.

Work of the Coal-to-Oil Laboratories and Pilot Plants at Bruceton and Pittsburgh, Pa., during the calendar year 1948 is outlined as follows:

1. Process development on direct hydrogenation of coal and on the synthesis of liquid fuels from the gasification products of coal (hydrogen and carbon monoxide) -

A basically new approach to the problem of synthetic-liquid-fuel production by direct hydrogenation of coal is under investigation. This departure from the conventional coal-hydrogenation process is based on the idea of rapid conversion of coal to distillable oil, gas, and coke at moderate pressures and relatively high temperatures. The conversion of as much as 50 percent of the coal to coke is not disadvantageous, because about as much coal is needed for fuel as is liquefied in coal-hydrogenation processes. The results of laboratory-scale tests have been encouraging; but the engineering problems are very difficult, and much pilot-plant development work must be done.

The internally cooled (by oil circulation through a bed of catalyst granules) process for liquid fuels by synthesis of carbon monoxide and hydrogen has been greatly improved during the past year, and relatively cheap, durable catalysts have been found for the process. A second process is in the pilot-plant stage of development. In this process, the finely powdered catalyst is suspended in a high-boiling oil and the synthesis gas bubbled through the suspension.

2. Laboratory studies on the composition of synthetic liquid fuels and on the important physical and chemical factors involved in synthetic liquid fuel process -

Industrially valuable byproducts of the direct hydrogenation of coal are phenolic compounds used in the manufacture of plastics. By means of infrared spectroscopic analysis and an ingenious countercurrent distribution of the phenolic fraction between two immiscible solvents, quantitative analysis of the mixture has been accomplished and procedures developed for separation into pure components.

The products of gas synthesis consist chiefly of straight-chain, normal hydrocarbons, with a minor amount of branched hydrocarbons. Infrared and mass-spectrometer techniques aided in determining the exact isomeric composition of the branched hydrocarbons. This information is of critical scientific importance in ascertaining the mechanism of the synthesis and also of industrial significance because the octane number of the gasoline fraction depends markedly upon the isomeric composition.

For the direct hydrogenation of coal, extensive laboratory tests in small, high-pressure vessels have provided critical information on the chemistry of the primary liquefaction. For gas synthesis, rate measurements in laboratory reactors, X-ray, and magnetic studies of catalysts have resulted in clearer understanding of the nature of the catalytic processes involved.

3. Testing of a vortex combustor for gasification of powdered coal (this project is being conducted in cooperation with the Combustion Research Section of the Coal Branch) -

The vortex combustor is a device designed for combustion of powdered coal. It is unique in that the heat evolved per cubic foot per hour is about 100 times that of most other combustion devices. A study is being made of its application to gasification of coal for synthesis-gas production in manufacture of liquid fuels by the modified Fischer-Tropsch or gas-synthesis process. During the year, the coal feed and other parts of the unit have been redesigned and rebuilt. The results thus far are encouraging, but more development work must be done to critically evaluate the possible application of this device for synthesis-gas production.

4. Reviewing, abstracting, and translating all available information on synthetic-liquid-fuel processes and maintaining complete files and reference service on foreign synthetic-liquid-fuel documents -

Critical evaluation of all captured German documents on the Fischer-Tropsch process is about 75 percent completed. The results of this evaluation and of all research work done in the United States on this process will be published in the near future. Similar evaluation of data on coal hydrogenation and on coal gasification have been begun.

Synthesis of Liquid Fuels from Hydrogen and Carbon Monoxide (Fischer-Tropsch and Related Processes)

Process Development

Pilot-Plant Operations

Operation of the internally cooled (by oil circulation) process using a completely flooded bed of granular iron catalyst has been found feasible if the physical structure of the catalyst is such as to avoid disintegration by hydraulic action of the oil. Precipitated and pelleted iron catalysts are not sufficiently robust, but sintered or fused iron oxides are satisfactory. Using a doubly promoted (with potassium and magnesium oxides) synthetic-ammonia-type catalyst, several runs were made in the pilot plant (figs. 26-28) after moving it from its Pittsburgh location to Bruceton, Pa. These operations varied in duration from several weeks to several months and were planned to ascertain the optimum operating conditions. Although not yet completely determined, these conditions now are reasonably well known, and the present operation will yield catalyst durability as well as product-quality and product-distribution data.

The internally cooled process, as now visualized, will operate with largely conductive (by oil circulation) rather than evaporative cooling. Operating temperatures will be in the range 210° to 325° C. and pressures 300 to 450 pounds per square inch. Product distribution can be controlled within fairly wide limits by selecting catalyst and operating conditions. Control of the usage ratio of hydrogen to carbon monoxide is feasible by proper pretreatment of the catalyst and to a limited extent by adjustment of operating conditions.

Cost estimates on Fischer-Tropsch processes, starting with coal as the source of carbon, show that a very large fraction of the cost of production of liquid fuels is the cost of synthesis gas production and purification. It is apparent, therefore, that, for industrial purposes, such processes must use the synthesis gas in a very efficient manner; that is to say, only a minimum of gaseous hydrocarbons should be produced and the usage ratio of hydrogen to carbon monoxide adjusted by selection of catalyst and operating conditions so that it is identical with the ratio in the cheapest synthesis gas. Although the internally cooled, oil-circulation process is better than the fluidized-iron-catalyst process, so far as concerns low methane production and suitable usage ratio of hydrogen to carbon monoxide, it does produce more methane than the "oil-catalyst slurry" process. In the latter process, a powdered catalyst

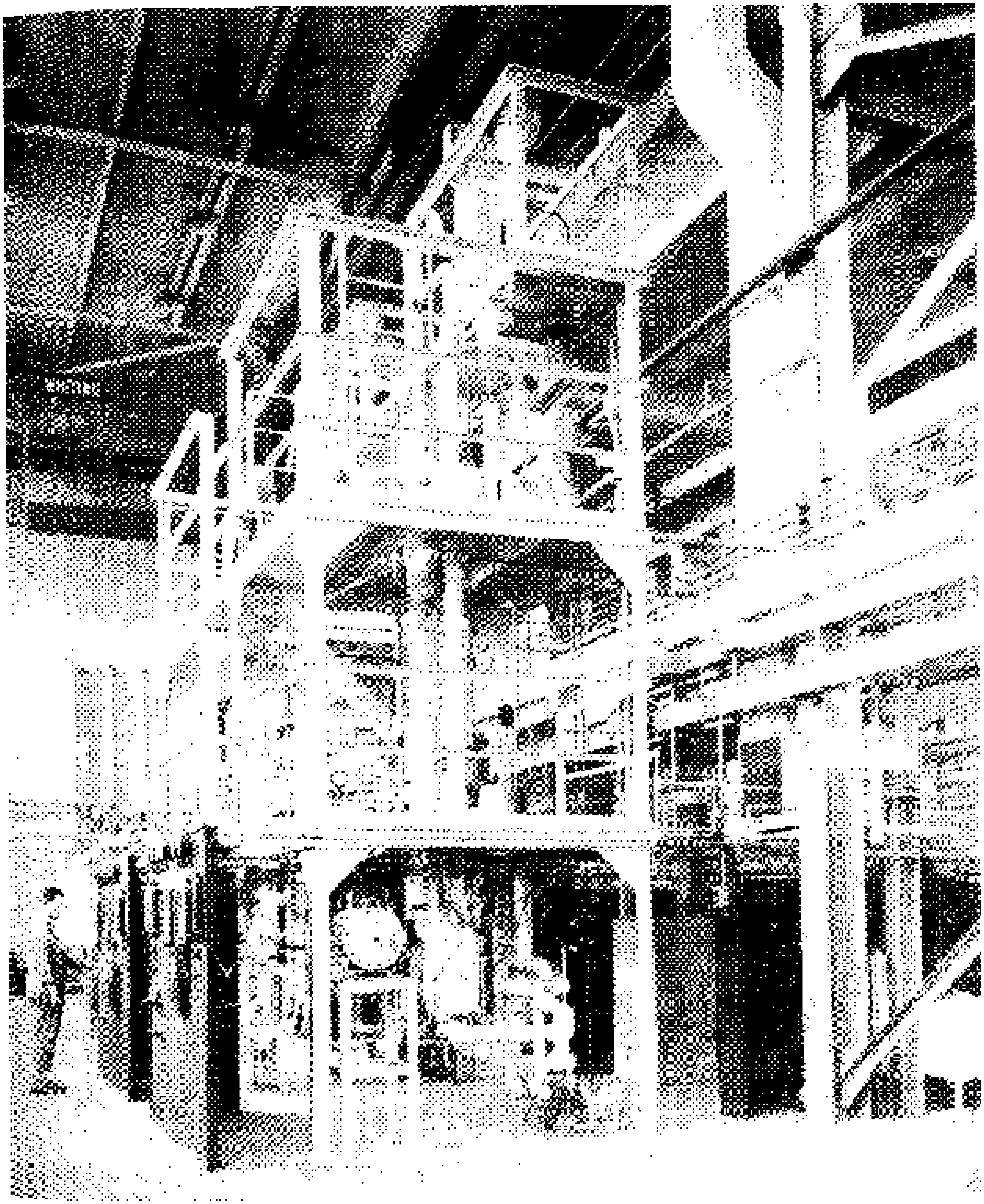

Figure 26. - Pilot plants for internally cooled (by oil circulation) process for synthesis of liquid fuels from hydrogen and carbon monoxide.

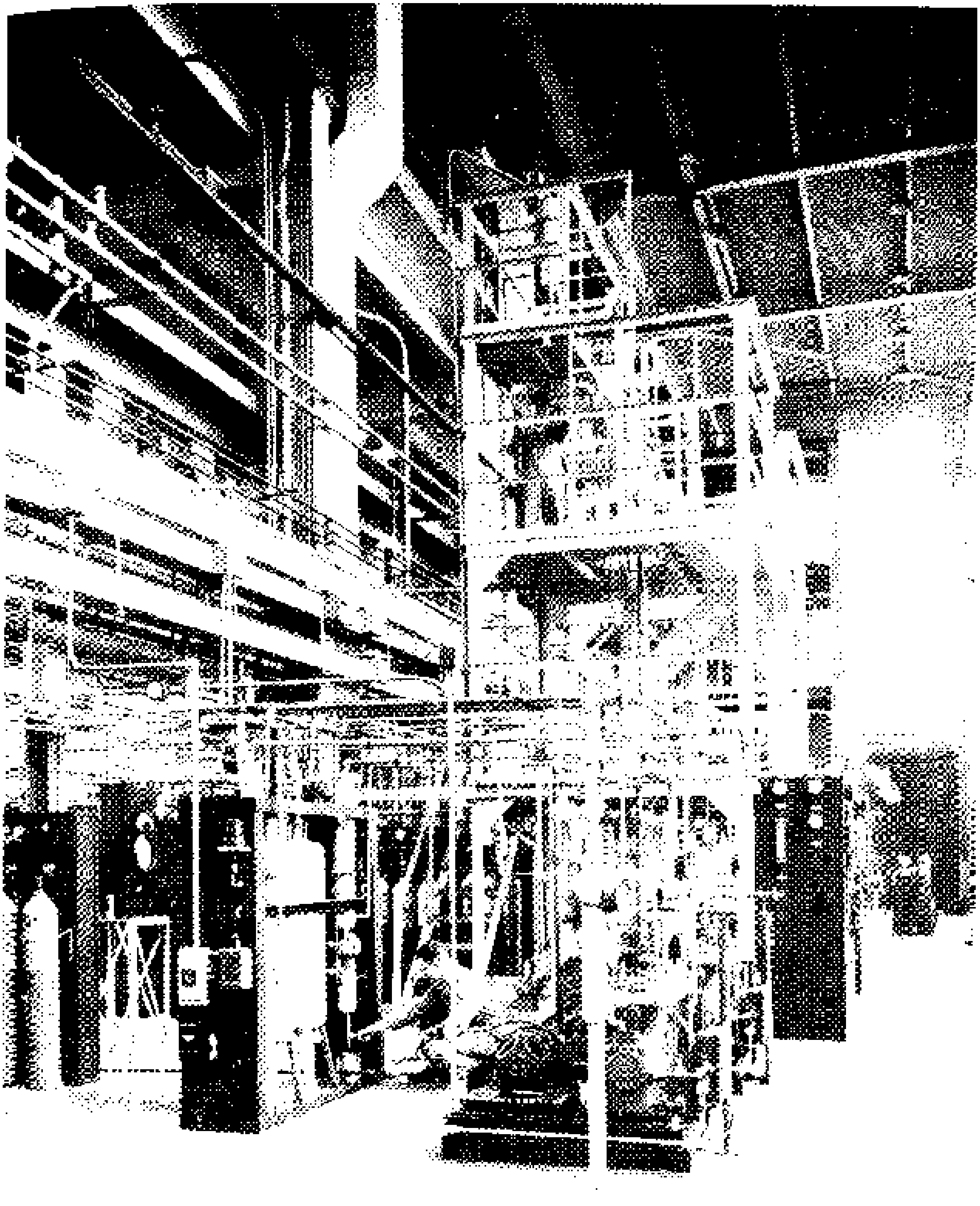

Figure 27. - Pilot plants for internally cooled (by oil circulation) process for synthesis of liquid fuels from hydrogen and carbon monoxide.

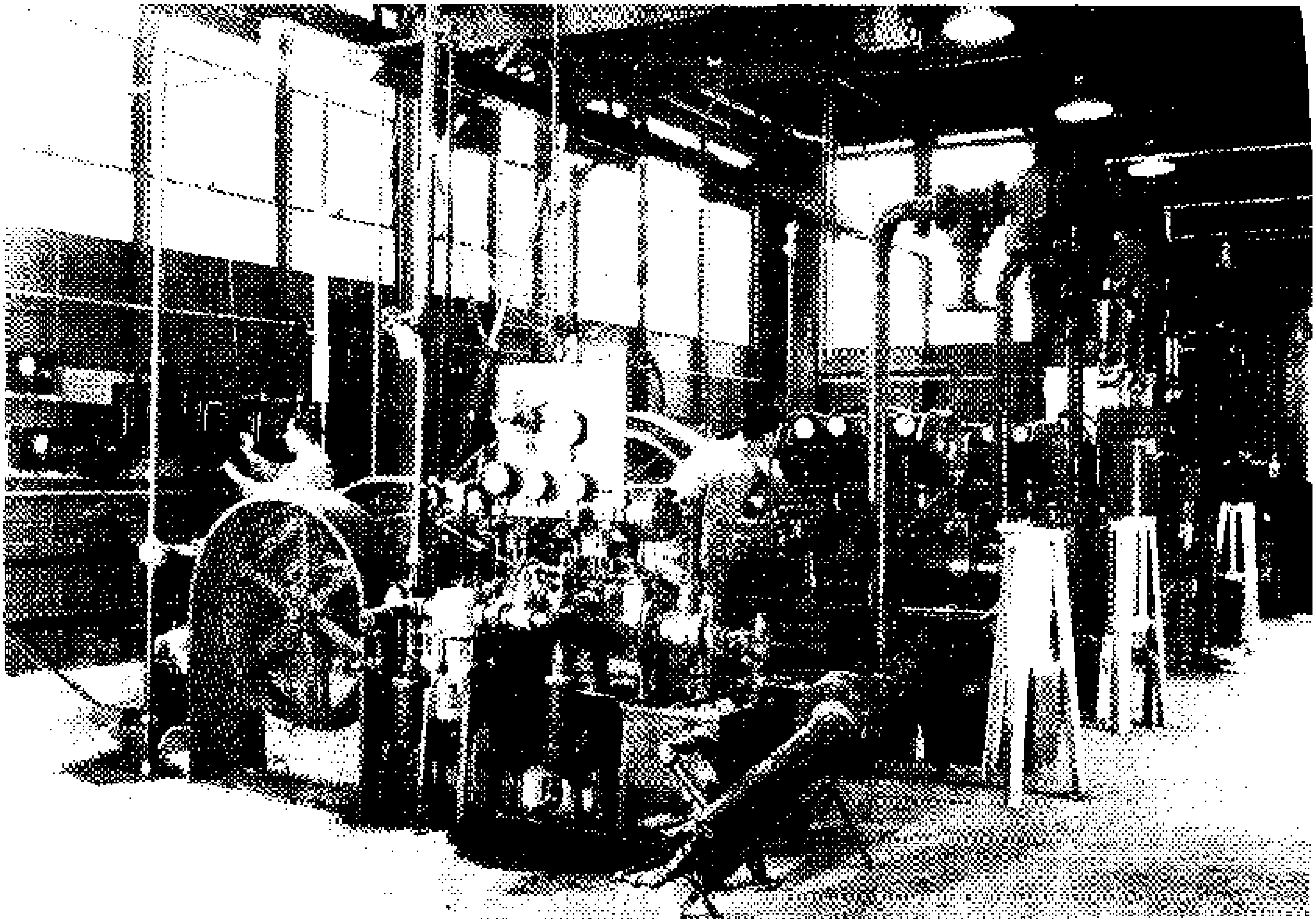

Figure 28. - Fischer-Tropsch compressor house.

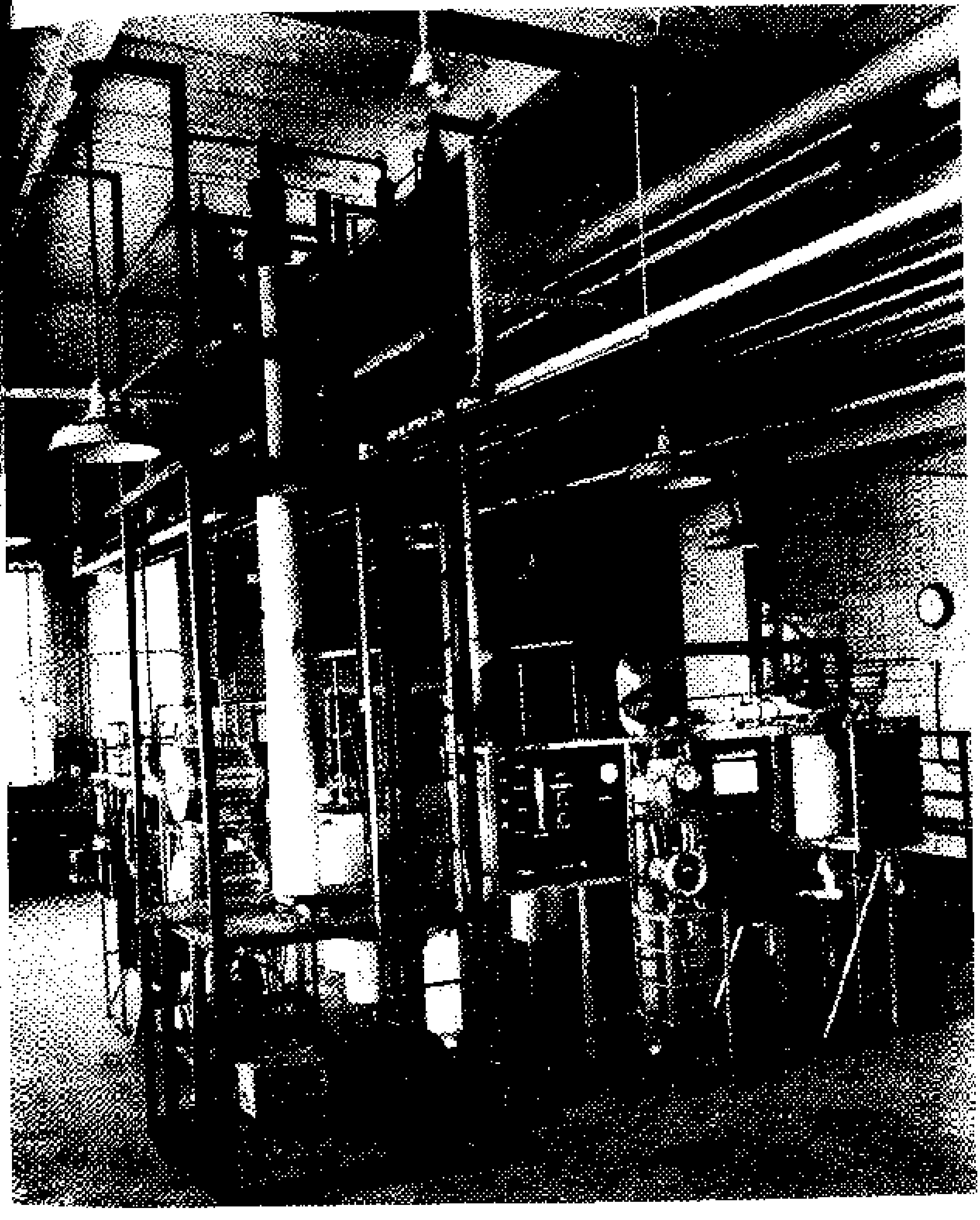

Figure 29. - Fischer-Tropsch catalyst-oil slurry-process reactor.

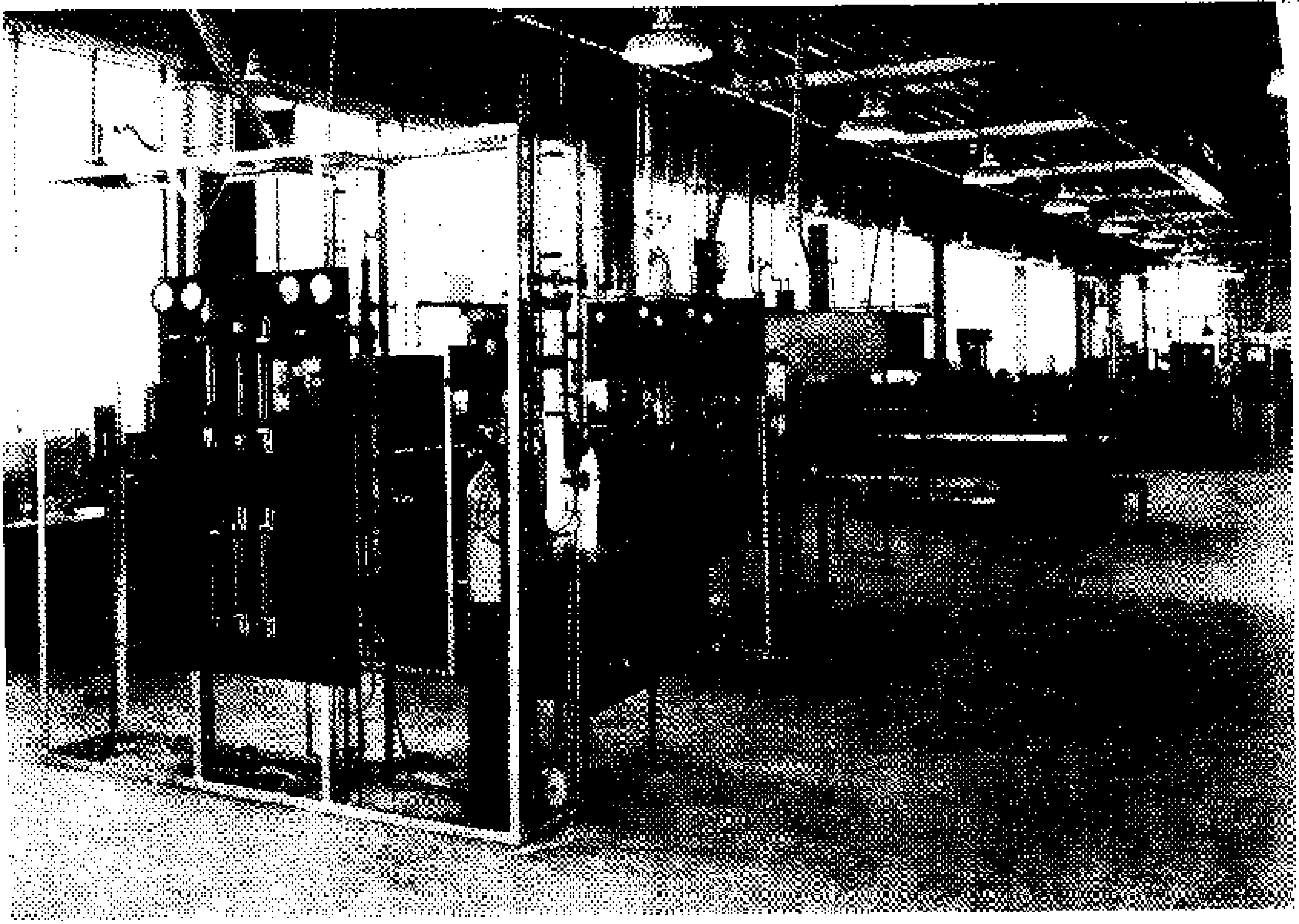

Figure 30. - Fischer-Tropsch process-development laboratory.

is suspended in an oil that is nonvolatile under operating conditions, and the synthesis gas is bubbled up through this suspension. Laboratory and pilot-plant studies of this process were conducted during the past year (see fig. 29). In this process the fraction of carbon monoxide converted to gaseous hydrocarbons is very low (only about one-fourth of that for other processes), and the boiling range of the liquid product can be varied over wide limits by selection of catalyst and operating conditions. The oil-catalyst slurry process has the additional advantage of possible continuous removal of partly spent catalyst and continuous introduction of regenerated or fresh catalyst.

Laboratory Scale

Laboratory experiments on the internally cooled, oil-circulation process are being conducted to determine the mechanical stability of new catalysts and the necessary type of control of wax concentration in the recirculated oil. Progress is being made toward early solution of the problem of very cheap, durable, and adequately active catalysts for the internally cooled process. Because of the relatively expensive and difficultly reproducible nature of the fused, synthetic-ammonia-type iron catalyst, work was begun on the use of readily available iron ores and industrial byproduct iron oxides for catalyst manufacture. Starting with either finely divided magnetite ore concentrated by magnetic separation or mill scale from the steel industry, active and durable catalysts were prepared. The preparation consisted in making a thick paste of the finely powdered iron oxide with an aqueous solution of the nitrates of promoters such as aluminum, potassium, magnesium, and calcium, extruding the paste into small rods about 3/16- by 1/2-inch, drying, sintering at 500° to 600° C., crushing to 8- to 10-mesh, and reducing with hydrogen. Catalysts so prepared were found to be much more active than the fused synthetic-ammonia type. They were, however, not resistant enough to mechanical disintegration by the hydraulic action of the circulating oil in the internally cooled reactor. Improved mechanical stability is being sought by the addition of binders, such as clay and silica gel. The cost of these catalysts will not exceed about 5 cents per pound.

Measurements of the temperature and pressure coefficients of the synthesis have been completed. Although the temperature coefficient is about the same as for cobalt catalysts, the pressure coefficient is much higher. Prolonged laboratory durability and activity tests are in progress to determine the effect of different degrees of reduction of iron catalysts and of impurities such as carbon oxides and water vapor in the hydrogen gas used for reduction (see fig. 30). The results indicate that a high degree of reduction is essential for the fused iron oxide catalysts and that the hydrogen used for reduction must be quite free of water vapor to obtain the most rapid rate of reduction at a given temperature. The presence of 1 to 2 percent of carbon monoxide appears to be beneficial so far as early activity of the catalyst is concerned.

Reduction of fused-iron catalysts is a relatively expensive step because relatively pure hydrogen is required and the time and temperature (about 450° C.) of reduction necessitate a special installation for this operation. Precipitated catalysts can be inducted into the synthesis by treatment with synthesis gas at synthesis temperatures (about 250° C.). The unreduced fused-iron catalyst has only a very small surface area and little or no pore volume. Reduction at 450° C. provides a system of pores and fissures and an increased surface area. The unreduced precipitated catalysts have a relatively large area and pore volume and do not need extensive reduction before use in the synthesis. The sintered catalysts prepared from iron ores or mill scale resemble the fused catalysts so far as reduction is concerned. It may be possible, however, to develop a catalyst prepared from iron ores that can be inducted in a manner similar to that used for precipitated catalysts. Laboratory experiments are in progress toward this objective.

Laboratory work on the oil-catalyst slurry process included a large number of tests to determine the effects of rate of gas flow and of mechanical agitation on the distribution of the catalyst powder. Earlier experiments had shown the necessity of uniform distribution of the catalyst; even a small percentage of settling in any part of the reactor results in a marked decrease in activity and durability. Two continuously operable laboratory units with provisions for mechanical agitation have been built for catalyst testing purposes. To measure accurately the effect of the area of the gas to liquid interface, a study has been begun using a finely divided spray or fog of oil-catalyst slurry injected into the synthesis gas. In addition to determining the importance of the gas to liquid interfacial area, these tests should show whether a spray or fogging type of operation is preferable to the bubbling of synthesis gas up through a column of oil-catalyst slurry.

Analysis of Iron Catalysts

While, as indicated in last year's report, little or no metal carbide is formed when the synthesis is conducted on cobalt catalysts, and extensive precarbiding greatly reduces the activity of these catalysts, the reverse is true for iron catalysts. Precarbiding of iron catalysts prepared by precipitation from solutions of iron and promoter-metal nitrates yields very active catalysts. Where no precarbiding is done, iron catalysts form large amounts of iron carbide during the first few weeks of operation.

The X-ray diffraction patterns of the three forms of iron carbide were measured accurately. This information, combined with measurements of the magnetic properties (particularly the Curie points) of the same catalysts and our earlier similar measurements on the iron oxides, has provided the essential elements for analysis of iron Fischer-Tropsch catalysts by physical methods. Such analysis is being applied to the study of changes in the catalyst during its useful life (usually about 1 year).

Surface Areas and Porosity of Catalysts

Measurements of surface areas, pore volumes, and activated adsorption of carbon monoxide are being made on all catalysts tested (see fig. 31). Some limited correlations have been established between surface area and activity of cobalt catalysts. For iron catalysts that are fused or sintered, the desirability of complete reduction with hydrogen before use in the synthesis is best-explained by the creation of a system of pores and fissures by the reduction.

Analysis of Gasolines

The isomeric composition of Fischer-Tropsch hydrocarbons boiling in the gasoline range (up to 200° C.) is being carefully measured, using the infrared and 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, in the products from both cobalt and iron catalysts, 10 to 15 percent of singly branched hydrocarbons is present. The branching usually is at the second or third carbon atom from the end of the chain. No branch larger than a methyl group and no multiply-branched molecules have been found.

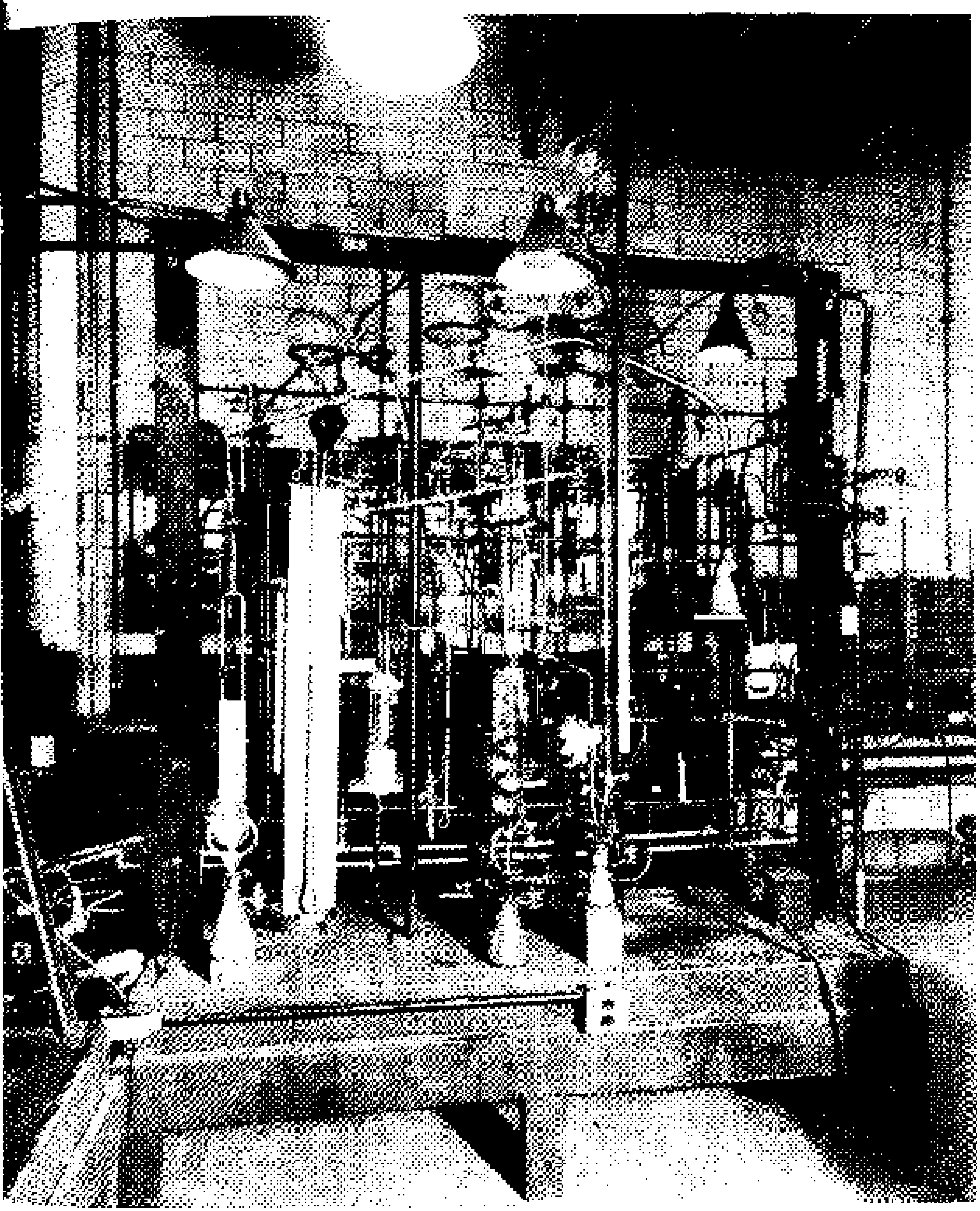

Figure 31. - Equipment for measuring surface areas of catalysts.

The olefins in gasoline from cobalt catalysts contain 20 to 30 percent olefins with the double bond between the first and second carbon atom of the chain and 70 to 80 percent of olefins with the double bond between the second and third and the third and fourth carbon atoms. The position of the double bond in olefins in gasoline from iron catalysts is the inverse of that from cobalt catalysts; 70 to 80 percent of the iron-catalyst olefins have the double bond between the first and second carbon atom.

The scientific and practical significance of these analytical data merits some comment. The data show that the octane number of Fischer-Tropsch gasolines depends largely upon the types and amount of olefins present, as the types and amounts of branched-chain saturated hydrocarbons are such that they add very little to the octane rating.

The impact of the analytical data is far-reaching so far as the mechanism of the synthesis is concerned. The absence of more than traces of multiply branched hydrocarbons and of branches longer than a methyl group cannot be explained by a mechanism that assumes the formation of long chains by polymerization of methylene groups. It appears necessary to assume that, after methylene groups are formed by reduction of chemisorbed carbon monoxide, alcohols are formed by reaction of the methylene groups with carbon monoxide and hydrogen. Subsequent dehydration of the alcohols yields olefins that react further with carbon monoxide and hydrogen yielding alcohols of higher molecular weight. At various stages in this reaction chain, olefins are either desorbed as such or hydrogenated to form saturated hydrocarbons. This mechanism is in accord with data on the quantitative analysis of the products and with data that show that alcohols actually are the precursors of the olefins in the synthesis.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Pilot-Plant Operations

The installation of two pilot plants, one for the first or liquid-phase stage and one for catalyst testing in the second or vapor-phase stage, has been completed. Some views of the liquid-phase plant and one of the vapor-phase unit are shown in figures 32 to 36.

The liquid-phase plant has a capacity of about 10 gallons and the vapor-phase unit of about 3 gallons of liquid product per day. Operation of both plants will be started shortly and be concerned with tests on raw materials, catalysts, and procedures to be used in the larger demonstration plant at Louisiana, Mo.

Laboratory Scale

The cost of compressed hydrogen constitutes about 50 percent of the total cost of liquid fuels prepared by hydrogenation of coal. Another large fraction of the total cost is capital charges on the investment and maintenance of the equipment. The program of process development is centered about possible reductions in these two large cost items.

Previously, industrial hydrogenation of coal has been effected by the use of almost pure hydrogen. Laboratory experiments at Bruceton have shown that it is possible to replace hydrogen by water gas under appropriate operating conditions. An estimate of the decreased cost to be expected from this discovery is being made by the