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

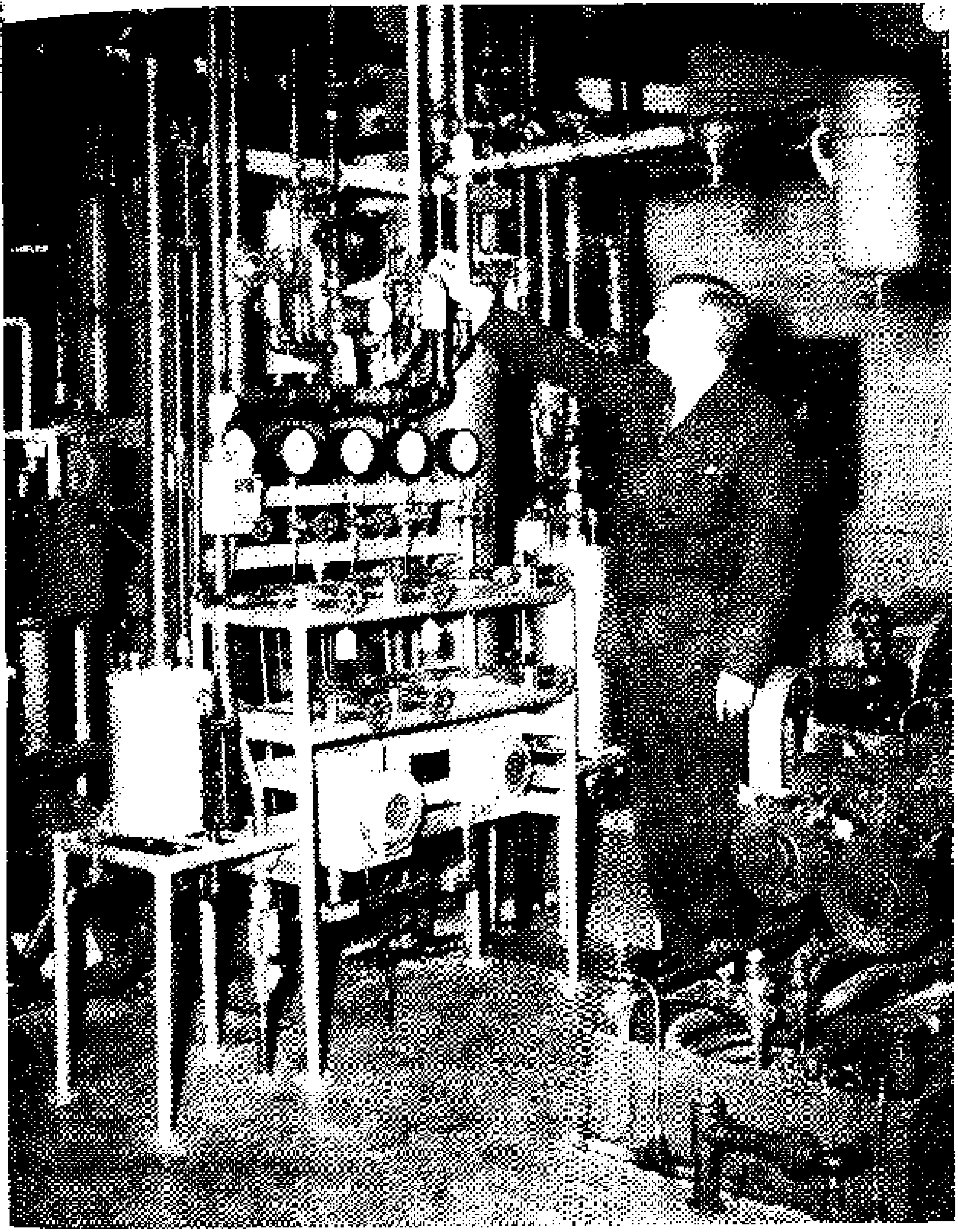

Figure 32. - Hydrogen compressor-valve manifold for coal-hydrogenation pilot plant.

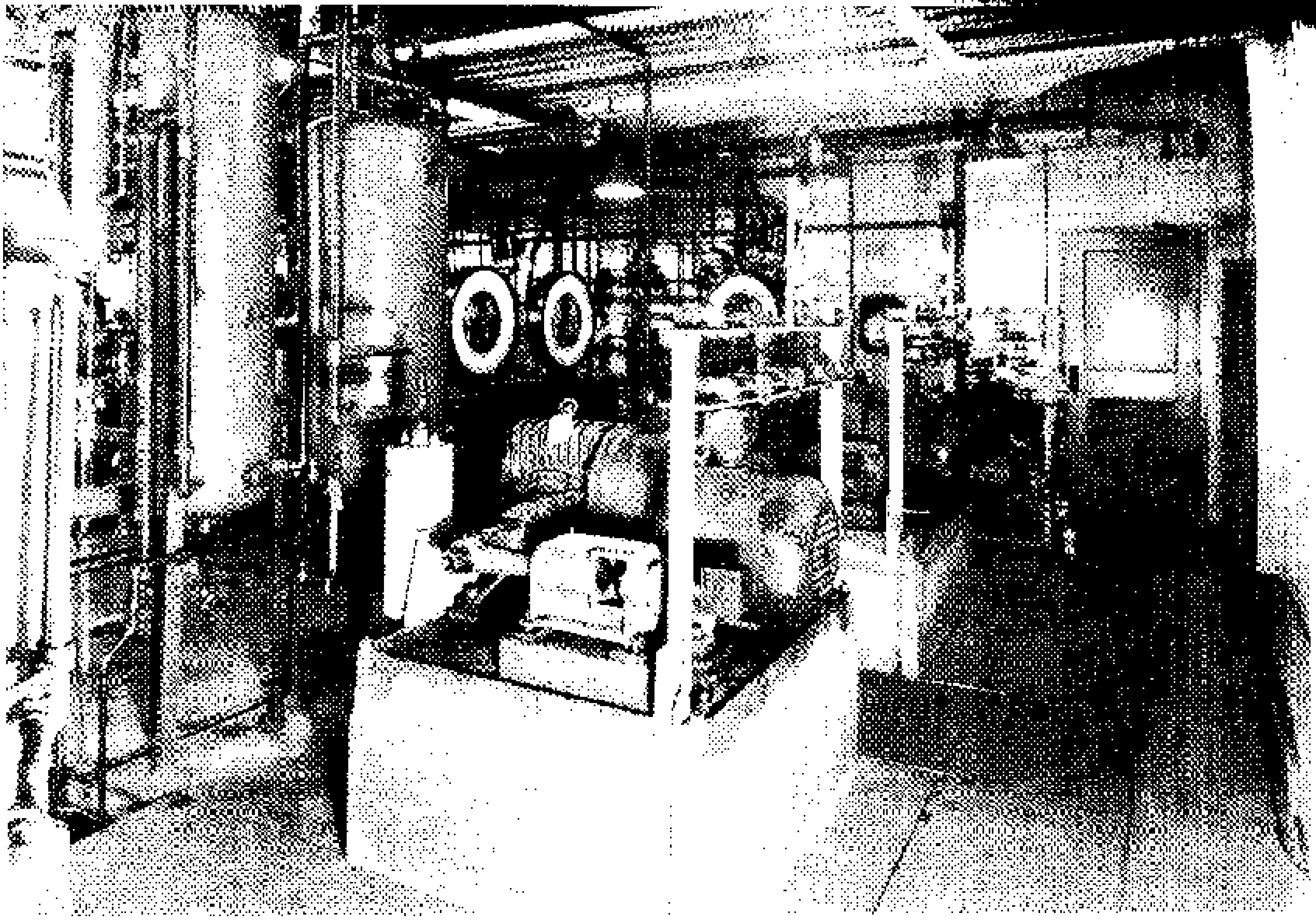

Figure 33. - Liquid pumps, coal-hydrogenation pilot plant.

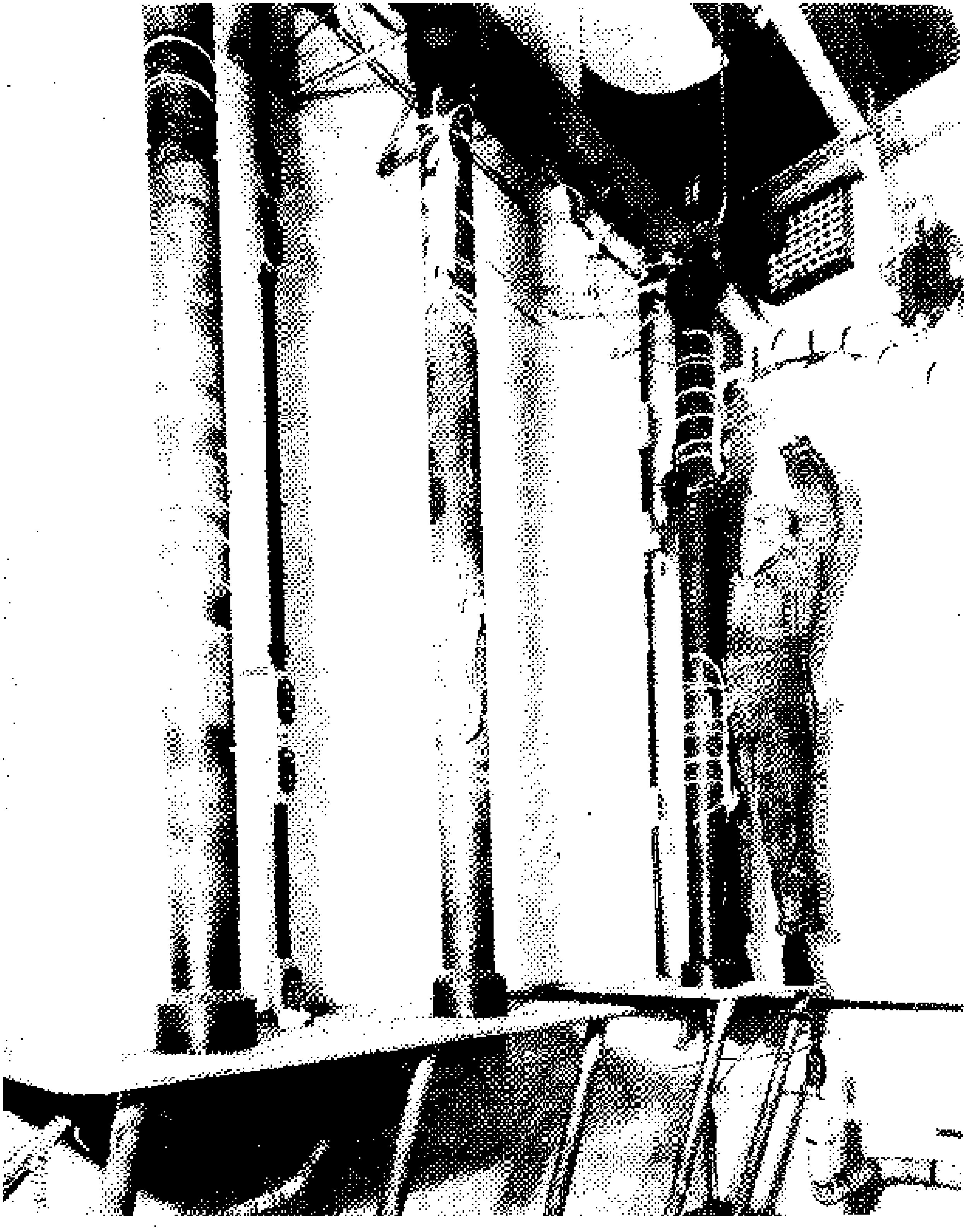

Figure 34. - Coal-hydrogenation liquid-phase reactors.

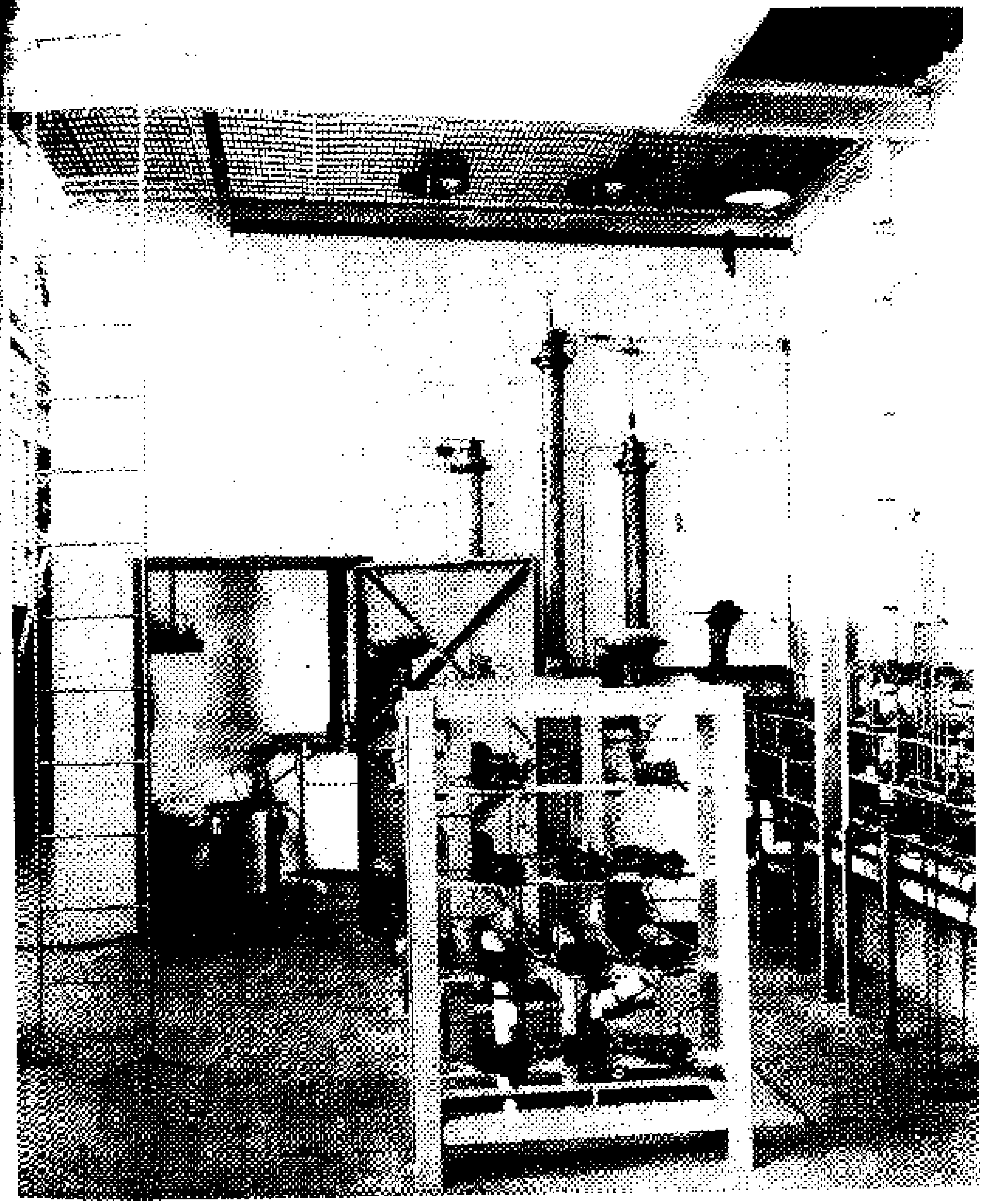

Figure 35. - Liquid-phase coal-hydrogenation pilot plant. Preheater at left in hot stall, gas scrubbers on wall behind door, and control valves in foreground and on wall at right.

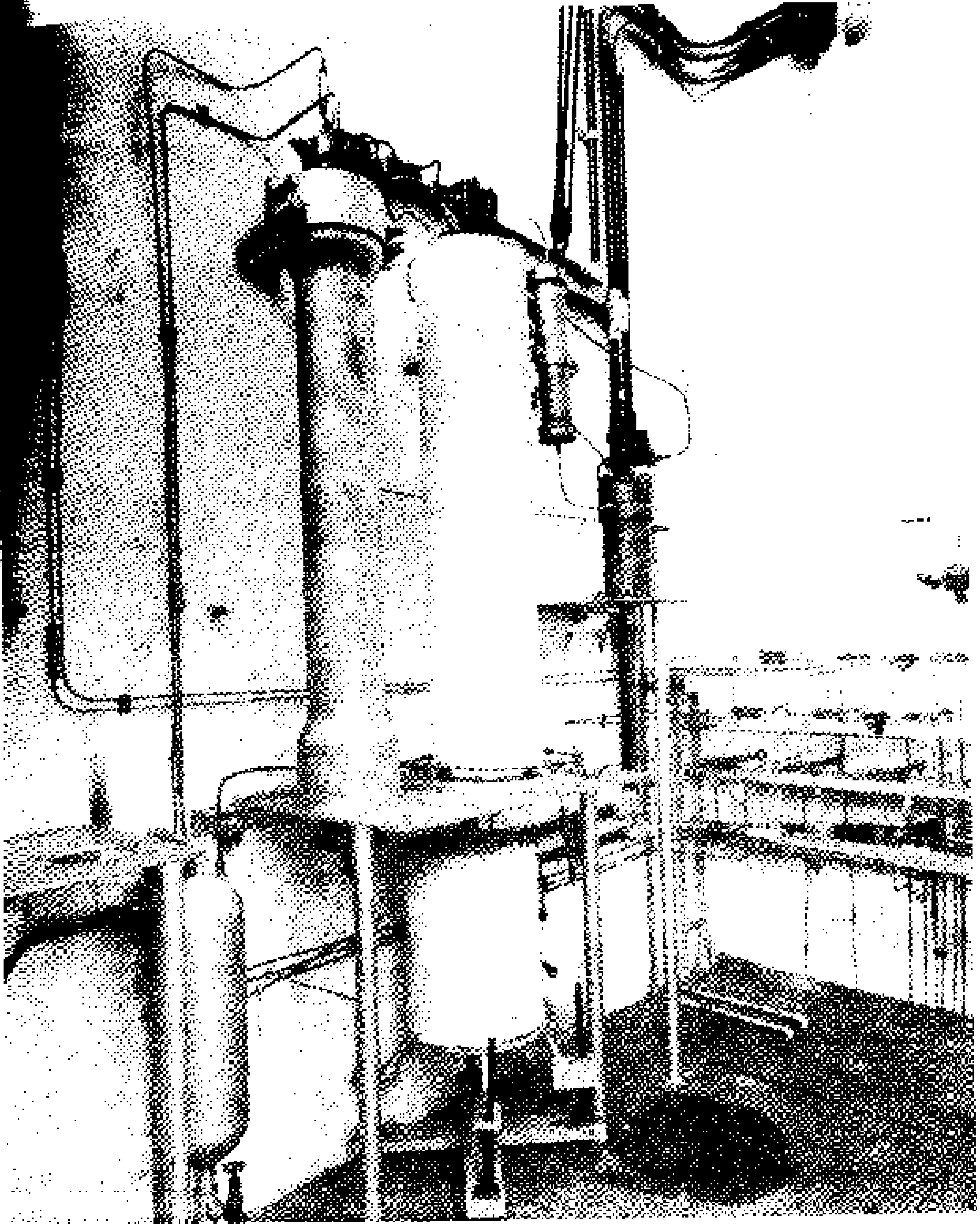

Figure 36. - Coal-hydrogenation vapor-phase catalyst-testing unit.

demonstration-plant staff at Louisiana, Mo. Another procedure for reducing the cost of hydrogen consists in the use of byproduct hydrocarbon gases. These may be obtained under pressure of 500 to 600 pounds per square inch, reacted with steam at that pressure, and the resulting mixture of hydrogen and carbon dioxide washed with water under pressure. In this way, the initial compression of hydrogen can be avoided, and with a relatively small sacrifice in oil yield enough byproduct hydrocarbons can be formed to supply all the hydrogen necessary for the process. An estimate of the reduction in cost of plant installation and operating cost to be expected from the use of byproduct hydrocarbon gas for hydrogen production also is being made by the demonstration-plant staff.

A third procedure, which should result in a lower cost of hydrogen as well as of equipment, consists in passing about twice as much coal through the hydrogenation plant as is hydrogenated. Thus about one-half of the coal feed is converted to oil and gas and the other half to coke. The latter is burned for steam and power production. In this way, all of the available hydrogen in that half of the coal feed which is converted to coke appears in the oil and gas. A laboratory-size reactor for studying this possible process has been built and operated (see fig. 37). It is so arranged that a continuous feed of powdered coal is supplied from a pressurized hopper, and a continuous stream of preheated hydrogen keeps the powdered coal in suspension. The volatile reaction products are carried out in the stream of hydrogen gas. When a noncaking subbituminous coal is used, the coke produced is kept in suspension in the gas stream. The first few experiments were orienting in nature, but enough data were obtained to show that at 450° to 600° C. with hydrogen at 500 to 1,000 pounds per square inch pressure, about 25 percent of the ash- and moisture-free coal appears as distillable oil, 25 percent as gaseous hydrocarbons, and 50 percent as coke. The contact time at the higher temperature is 20 to 30 minutes.

Although it is apparent that a possible new and cheaper coal-hydrogenation process may be developed, there are many severe engineering difficulties. The feeding of dry coal by a pressurized hopper is an expensive operation. This difficulty has been solved by developing satisfactory equipment for pumping a mixture of powdered coal and a volatile vehicle such as water or a light oil. Subsequently, the vehicle will be rapidly vaporized or flashed off as soon as the mixture enters the pressurized reactor. Such a coal-feeding device necessitates efficient heat exchange to provide the heat of vaporization of the vehicle. The dry-coal powder would then be brought into contact with a stream of preheated hydrogen so that a uniform suspension of coal in the gas stream is obtained. The discharge of the coke "breeze" from the reactor probably can be engineered using conventional plug-type valves and pressure let-down hoppers without excessive loss of energy.

Combination of several of these suggested procedures may result in a much cheaper process. This might be effected by converting byproduct hydrocarbon gases under pressure to water gas and rapid conversion at moderate pressure of dry powdered coal in suspension in flowing water gas to distillable oil, gas, and coke, followed by use of the coke for steam and power production.

In the 1947 report, work was described on the steam stripping of coal-hydrogenation heavy-oil slurry, as obtained in the conventional Bergius-I. G. process. A photograph and description of the apparatus were included. In figure 38 a diagrammatic sketch of the equipment is presented. This project was completed in 1948. Heavy-oil let-down (H.O.L.D.), the solids-containing product of coal hydrogenation, was subjected to treatment with superheated steam in a continuous process. The effects of steam temperature (350° to 600° C.) and separator temperature (250° to 400° C.) on the oil yield and the distribution of the constituents of the H.O.L.D. (oil, asphalt,

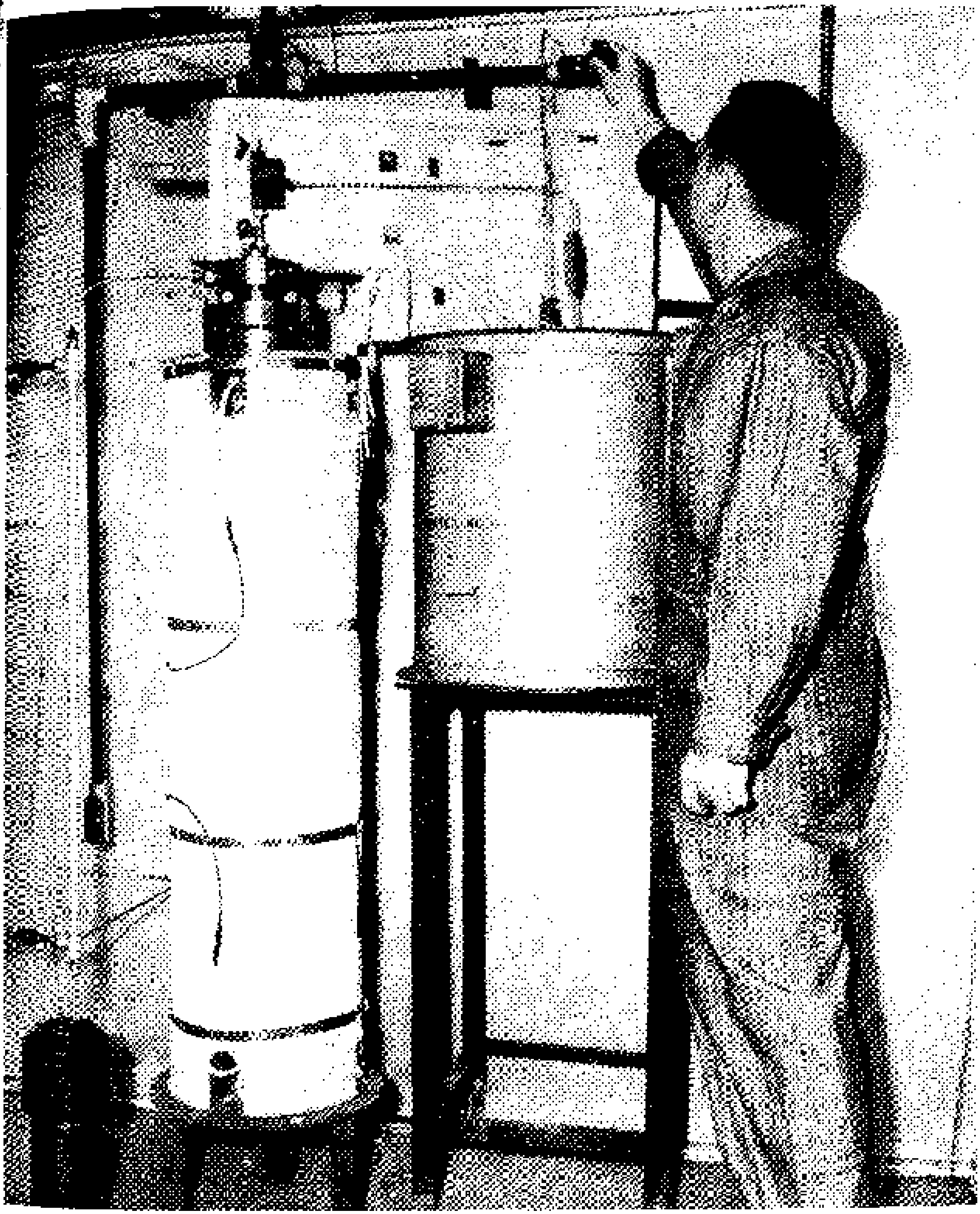

Figure 37. - Reactor for powdered coal in suspension in flowing hydrogen gas.

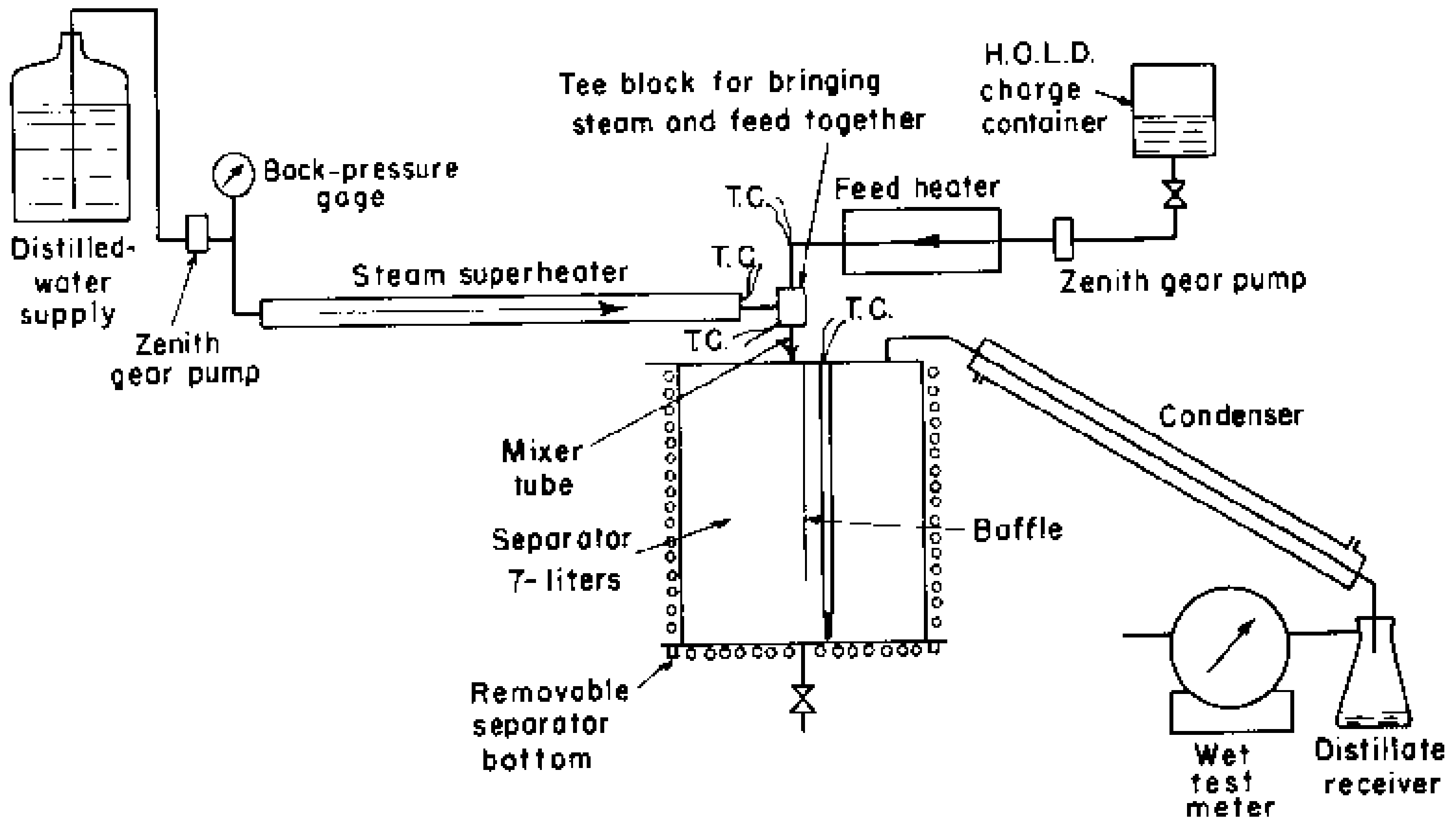

Figure 32. - Apparatus for steam stripping of heavy-oil let-down.

and benzene-insolubles) in the overhead product and residue were evaluated. Separator temperature exerted the greater effect on oil yield, asphalt in overhead product, gas formation, and the amount of additional benzene-insolubles formed. Benzene-insolubles did not appear in the overhead product in appreciable amounts. The highest yield of overhead product was 67 percent by weight of the feed and was attained under conditions of 500° C. steam, 2:1 weight ratio of steam to feed, 325° C. feed temperature, and 400° C. separator temperature. The overhead product contained all of the oil plus 44 percent of the asphalt present in the feed.

Basic Laboratory Research

The absence of a vehicle or solvent does not affect the rate of liquefaction of bituminous coal, but the amount of asphaltic material (insoluble in n-hexane but soluble in benzol) produced is much less in the absence of solvents. In laboratory small-autoclave experiments, it has been found that, in the absence of a vehicle, the amount of asphaltic material per unit of liquefaction decreases rapidly with increasing hydrogen pressure in the range 1,000 to 10,000 pounds per square inch, from about 0.3 to 0.1. The effects of contact time and temperature on rate of asphalt hydrogenation were measured. At 400° C. and 5,000 pounds per square inch pressure the rate of hydrogenolysis of the asphaltic material is very low, but at the same pressure it increases rapidly with temperature so that at 430° C. the rate is high enough for a practical coal-hydrogenation process. These rate measurements, combined with similar determinations of the rate of hydrogenation of specially prepared 100-percent asphaltic material from hydrogenation of coal, indicate the following mechanism for the primary reactions:

The primary reaction in coal liquefaction by hydrogenation is the production of reactive fragments of the coal structure, having the same average molecular weight as the asphaltic materials. These fragments are then stabilized by the addition of hydrogen. The production of asphaltic material proceeds quite rapidly, even at relatively low temperatures (400° C.), while the subsequent hydrogenation of asphalt to oil and hydrocarbon gases requires higher temperatures. The fragmentation of the coal structure probably is associated with splitting of carbon-to-oxygen bonds and the conversion of asphaltic material to oil and gas, with the rupture of carbon-to-carbon bonds.

A section of laboratory research at Bruceton continues on the study of catalysis for the liquid-phase hydrogenation. The outstanding efficiency of tin as a catalyst for the first stages of coal hydrogenation persists under a great variety of conditions. Whatever type of vehicle is employed, in the absence of any vehicle and in a wide range of temperatures and pressures, tin is outstandingly more efficient than other catalysts. This is also true for a wide range in rank of coal, provided an adequate adjustment is made in the proportion of ammonium chloride used to neutralize the alkaline inorganic constituents of the coal. An excess of ammonium chloride of about 0.5 percent (of the coal) beyond the neutralization point is essential in all cases for maximum efficiency of tin. No satisfactory explanation of the unique character of tin has yet been found. Laboratory experiments designed to furnish such information are in progress.

Because of the scarcity of tin, it is necessary to employ more readily available and cheaper catalysts in practical coal hydrogenation operations. As may be seen from table 8, when a high pressure of about 9,000 pounds per square inch of hydrogen is used, the cheaper and more readily available iron compounds approach the high efficiency of tin.

TABLE 8. - Hydrogenation of Rock Springs, Wyo., high-volatile C bituminous coal

(In laboratory autoclaves at 450° C., 3,700 pounds per square inch initial (cold) hydrogen pressure (about 9,000 pounds at reaction temperature), in absence of any vehicle. Pyrex-glass liner used to avoid catalysis by metal walls)

Run no.	Catalyst	Liquefaction, percent	Asphalt per unit of liquefaction	Coal gasified, percent
859	-	70.9	0.43	17.8
861	1 percent Sn + 0.5 percent NH_4Cl	97.7	.07	11.6
865	0.1 percent Sn as $SnCl_2 \cdot 2H_2O$	87.8	.50	17.8
878	0.1 percent Sn (powdered)	82.4	.57	13.8
849	0.1 percent MoO_3	70.0	.43	16.6
881	0.1 percent Zn + 0.2 percent NH_4Cl	75.6	-	-
857	0.1 percent Fe as $FeSO_4 \cdot 7H_2O$	70.6	.51	15.6
866	1 percent Fe as $FeSO_4 \cdot 7H_2O$	84.7	.55	13.5
872	1 percent Fe (powdered)	64.7	.61	11.6
870	1 percent Fe as pyrite	83.1	.43	13.5
845	1 percent dried "red mud"[1]	83.5	.49	19.1

[1] Obtained through the courtesy of the Aluminum Co. of America. This material is the equivalent of Bayermasse, used extensively in German coal-hydrogenation plants.

The uncatalyzed hydrogenation resulted in a liquefaction of 71 percent. As usual, Sn (in the presence of Cl) proved to be outstanding. The "standard" catalyst, 1 percent Sn + 0.5 percent NH_4Cl, produced a liquefaction of 98 percent. 0.1 percent Sn, added as $SnCl_2$, resulted in 88 percent liquefaction, while 0.1 percent Sn powder was somewhat less effective. At a concentration of 0.1 percent, all other catalysts tried were relatively poor. Since it is desired to use an iron catalyst in the Demonstration Plant if it is possible, several iron catalysts were tested at a higher concentration level. Of these, dried "red mud"[2] seems most promising. At a total concentration of 1 percent, it is as effective as 1 percent iron in the form of $FeSO_4$ (that is, 2.7 percent $FeSO_4$), and it is probably considerably cheaper.

The extent of gasification varied in a random manner in these experiments, and it did not seem to be associated with the extent of liquefaction. The asphalt production was high in all cases except that in which 1 percent Sn was used.

Interest has been expressed in determining the susceptibility to hydrogenation of gilsonite, a naturally occurring asphalt. A sample of gilsonite from the Uinta Basin, Utah, was found to contain 2.0 percent benzene-insoluble material, 79.0 percent asphalt (soluble in benzene, insoluble in n-hexane), and 19.0 percent oil (soluble in n-hexane).

It had the following ultimate analysis:

Element	Weight, percent
H	10.13
C	85.16
N	3.18

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[2] Obtained through the courtesy of the Aluminum Co. of America. This material is the equivalent of Bayermasse, used extensively in German coal-hydrogenation plants.

Element	Weight, percent
C	1.18
S	.26
Ash	.09

Several batch autoclave runs were made to determine the ease with which gilsonite is hydrogenated under our standard conditions. The results are summarized in tables 9 and 10. The density of hexane-soluble material produced in a run identical with 726 was 0.911 g./cc. at 25.6° C.

TABLE 9. - Hydrogenation of gilsonite (50 g. gilsonite, 450° C., 1 hr.)

Run no.	Sn added, percent	NH_4Cl added, percent	Initial H_2, p.s.i.g.	Asphalt, percent[1]	Oil, percent[1]	Gasification, percent[1]	Benzene insolubles, percent[1]
762	-	-	1,000	14.2	61.0	14.2	11.4
749	1	-	1,000	17.6	56.8	17.4	9.2
750	-	0.55	1,000	16.8	51.8	19.8	13.6
726	1	.55	1,000	4.0	79.2	15.2	4.7
739	1	.55	1,500	2.2	79.8	17.6	2.9

[1] Based on weight of gilsonite only.

TABLE 10. - Volatile-oil production

Run no.	Percent converted to product distillable below 85° C., 1 atmos.	Percent converted to product distillable below 200° C., 2 mm. Hg
726	28.6	60.6
739	32.0	65.2

It is evident that the hydrogenation of gilsonite proceeds with ease, even in the absence of a catalyst. Unless both Sn and NH_4Cl are present, however, there is an appreciable production of benzene-insoluble material and a decrease in amount of asphalt converted to oil. Gas production was about the same in all the experiments. As may be seen from table 10, about 30 percent of the gilsonite is easily convertible to very volatile product, and up to 65 percent is converted to oil distillable below 200° C. at 2 mm. Hg (for an initial H_2 pressure of 1,500 p.s.i.g.). From this point of view, gilsonite would seem to be an excellent source of liquid fuels; unfortunately, the total reserves of gilsonite amount to only about one-half of one percent of the annual production of petroleum in the United States (see Chem. and Ind., vol. 58, 1939, p. 800).

Analyses for carbon and hydrogen in the benzene-insoluble, asphalt, and oil products from runs 749 and 750 and for Cl on the products from run 750 are listed in table 11.

TABLE 11. - Ultimate analyses of products

Run no.	Nature of product	Carbon, percent	Hydrogen, percent	Cl, percent
749	Benzene-insoluble	75.00	4.22	-
	Asphalt	85.03	7.19	-
	Oil	85.71	11.86	-
750	Benzene-insoluble	83.46	4.31	0.89
	Asphalt	86.27	7.48	.07
	Oil	86.57	11.46	.04

The low percentage of carbon for the benzene insolubles of run 749 is due to the ash (Sn) content. In general, the carbon and hydrogen contents of the three fractions are those that might be expected from the solubility characteristics. Of interest is the low Cl content of the oil and asphalt from run 750, in which only NH_4Cl was added as catalyst. This indicates that, although NH_4Cl (or HCl) may act to split asphalt, at least in the case of gilsonite, only a very small amount of Cl, at most, is chemically bound with the soluble products after hydrogenation. The Cl found in the benzene-insoluble product from run 750 is equivalent to only one-third of the Cl added as NH_4Cl, and it is almost exactly equivalent to the ash (taken as CaO) present in the original gilsonite.

Effect of Ultrasonic Waves

Because of possible unique scientific and even practical results, an ultrasonic wave generator has been installed to investigate the effect of ultrasonic energy on hydrogenation of coal. Under the proper conditions, irradiation of liquids with ultrasonic waves of high intensity causes a phenomenon known as cavitation, which consists of the rapid formation and collapse of vapor bubbles in the liquid. It has been calculated that, on collapse of the bubbles during cavitation, instantaneous local pressures of the order of thousands of atmospheres may be developed. At such pressures coal hydrogenation should proceed rapidly at moderate temperatures and with the cheaper and more available catalysts.

Rates of Primary Liquefaction

The nature of the initial steps in hydrogenation of coal have been difficult to ascertain because of our meager knowledge of the basic chemical and physical structure of the coal substance. During the past year an advance was made in precise measurement of the rate of liquefaction and oil production. Greatly improved analytical procedures that made possible very accurate mass balances indicated that it was desirable to repeat earlier rate measurements. The results show that, with increasing time of hydrogenation, the amount of asphaltic material (benzene-soluble, hexane-insoluble material) goes through a maximum and then decreases. The data fit accurately the following mechanism:

Asphalt is a primary product of coal liquefaction and an intermediate in the production of oil and hydrocarbon gases. The rate of the first step:

$$\text{Coal} \longrightarrow \text{asphalt,}$$

is much greater than the rates of the succeeding steps:

$$\text{Asphalt} \longrightarrow \text{oil, and}$$

$$\text{Asphalt} \longrightarrow \text{gaseous hydrocarbons.}$$

The rates of oil and of gas production are directly proportional to the quantity of asphalt present. The rate constants for these three steps, combined with results of organic chemical research on the structure of coal and the asphaltic material, has opened a road leading toward more detailed knowledge of the nature of the primary reactions and of possible radical improvements in the liquid-phase coal-hydrogenation process.

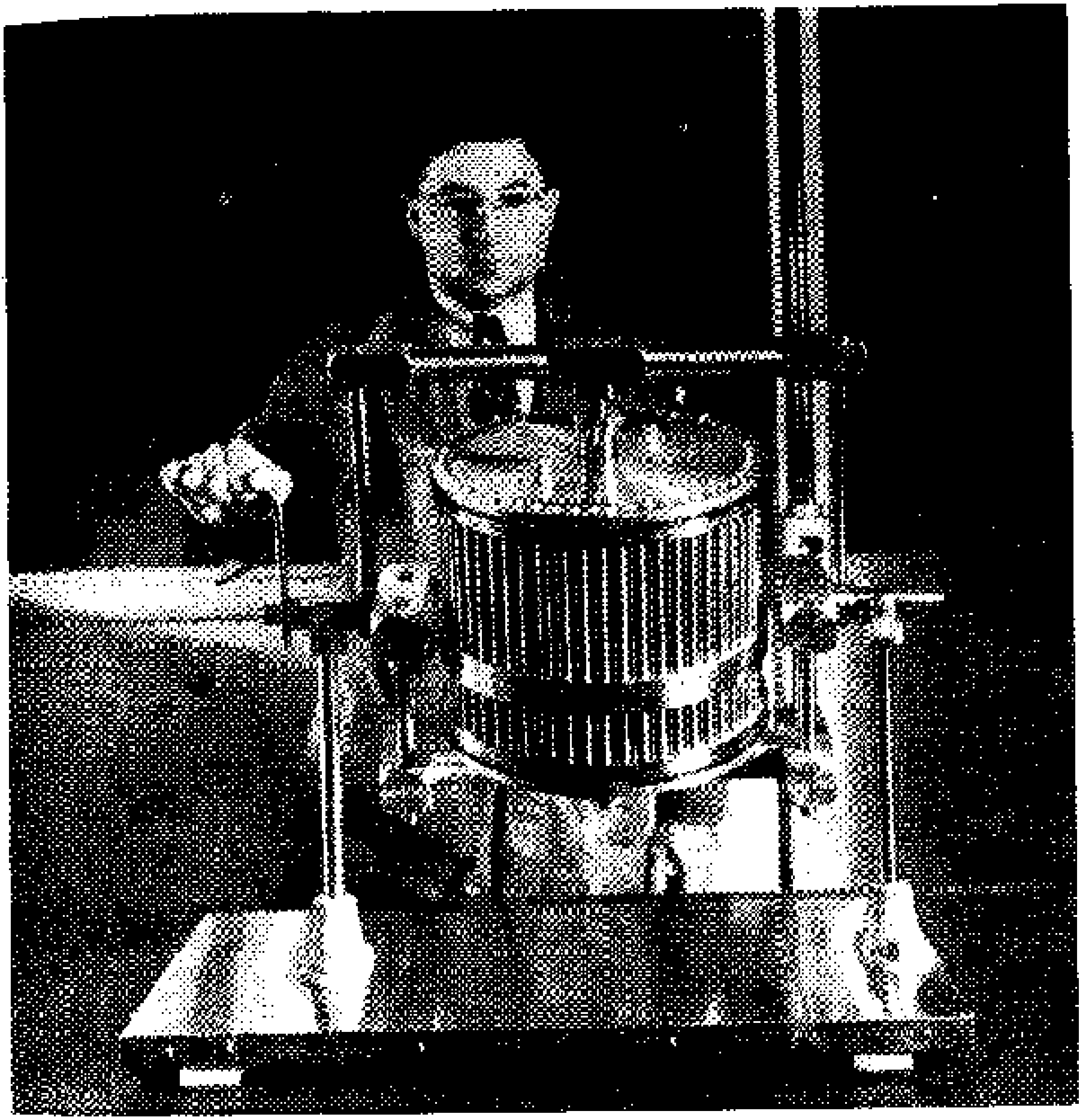

Figure 39. - Apparatus for countercurrent distribution between two immiscible solvents.

Analysis of Products

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

Further work was done on the separation and identification of the phenolic compounds in coal-hydrogenation oil.

The countercurrent distribution technique, which was developed for the separation and analysis of very small quantities of closely related compounds, such as antimalarial drugs and penicillin preparations, is being applied to the problem of determining the composition of complex tar-acid mixtures found in the heavy-oil product from the hydrogenation of coal (see fig. 39). In this procedure, a mixture of phenols is distributed between two immiscible solvents in successive countercurrent stages until separation into its components is achieved. In this way, it is possible to isolate individual or groups of closely related tar acids. Thus, for example, mixtures of C_8 tar acids, consisting of xylenols and ethylphenols, were separated. This technique is particularly valuable for mixtures, such as m- and p-cresol, that cannot be separated by other known physical methods.

Countercurrent distribution analysis has indicated that five compounds are present in the C_{10} tar-acid fraction of coal-hydrogenation oil. Further application on a larger scale has so far resulted in the concentration and isolation of one of the components in crystalline form.

As some of these components are present in substantial amounts in coal-hydrogenation oils, it is expected that the possibility for industrial-chemical utilization of tar acids from coal hydrogenation will be more clearly outlined by this research.

Separation of Constituents of Synthetic-Liquid Fuels

Installation of batch-distillation equipment has been completed (see figs. 40 and 41). Batches of 50 to 500 gallons of oil can be distilled in this equipment to provide large samples of gasoline Diesel oil or byproduct tar acids for practical tests and for precision separations to be conducted by the distillation group of the Organic Chemistry Section. The latter has been engaged in developing standards for vacuum distillation and in designing and erecting a number of precision stills. The service manifold for these stills is almost completed (fig. 42).

Analytical Control Laboratories

Analytical control work for the synthetic-liquid-fuels laboratory and pilot-plant operations is done in two standard-type laboratories (see fig. 43). Most of the gas analyses of the branch are made on the mass spectrometer. The number of such analyses frequently is 500 to 600 per month. To decrease the load on the existing mass spectrometer, a much smaller and less expensive mass spectrometer is under construction that can be used satisfactorily for analyses up to a molecular weight of 44. In this way, some time will be made available on the larger instrument for special research problem analyses.

Vortex Combustor Studies for Powdered-Coal Gasification

The construction of a vortex-type reactor and accessory equipment for studying the gasification of powdered coal by steam and oxygen was completed, and the unit was put into operation in March 1948.