The barrel-a-day Fischer-Tropsch pilot plant (figs. 28 and 29) is nearly completed. Various components of the equipment have been tested to assure satisfactory performance. The oil-absorption system, designed for the recovery of light hydrocarbons, has been modified slightly to allow the use of a potassium carbonate solution for the removal of carbon dioxide from the recycle gas. A small portion of the tail gas will be passed over activated charcoal to recover the light hydrocarbons and permit weight-balance calculations when operating the plant. Gas for the pilot plant is compressed in the equipment shown in figure 30.

Laboratory-scale Experiments

Catalysts. - Previous work in this laboratory and in other laboratories has shown that conversion of the iron in iron catalysts to an Fe_2C carbide by treatment with carbon monoxide or mixtures of hydrogen and carbon monoxide increased the catalyst activity in the Fischer-Tropsch synthesis. It was thought, therefore, that if the introduction of carbon into the iron lattice increases the activity of the iron catalyst, the introduction of another element - for example, nitrogen - also may enhance the catalyst activity.

The nitrides of iron cannot be formed by the action of molecular nitrogen, but they can be formed by the action of ammonia on iron. The nitride formed depends on the temperature, time, space velocity of ammonia, and the ratio of ammonia to hydrogen. As the rate of cracking of ammonia to nitrogen and hydrogen becomes appreciable at 450° C., temperatures of 350° to 385° C. are maintained. In this temperature range, a space velocity as low as 1,000 volumes of gas per volume of catalyst per hour permits an adequate ammonia-to-hydrogen ratio, and nitriding to an atom ratio N/Fe = 0.44 to 0.50 occurs in 4 hours.

Tests with iron catalysts treated in this manner have shown that these nitrided catalysts have significantly greater activity and life than corresponding reduced catalysts, and that the products from the nitrided catalysts are very different from those obtained with reduced catalysts. The nitrogen is only very slowly removed from the catalysts during the synthesis, and available data indicate that carbon replaces the nitrogen, whereas the ratio of total-carbon-plus-nitrogen atoms to iron atoms remains approximately constant. Nitrided catalysts appear to resist oxidation and deposition of free carbon in the synthesis. Thus, nitriding may be a practical and economical method of eliminating the difficulties of catalyst instability due to carbon deposition, oxidation, and related processes. The selectivity of the catalyst is changed significantly by converting the iron in the catalyst to ϵ-phase nitrides and nitriding is another way of increasing the versatility of the Fischer-Tropsch synthesis with iron catalysts.

The differences between the products from nitrided and reduced iron synthetic-ammonia-type catalysts were not a result of the different temperatures of operation and must therefore be related to some fundamental change in the catalyst surface. The enhanced activity of nitrided catalysts also may result, at least in part, from the lower-molecular-weight products formed by the nitrided catalysts. These products may be expected to desorb more readily than do the heavier products from reduced catalysts, thus increasing the effective surface area of the nitrided catalysts. It has been found, however, that a catalyst partly converted to γ'-phase nitride has a greater activity than a similar reduced catalyst, although the product distribution is not significantly different from that of the reduced catalyst, and thus, in this case at least, the increased activity is not due to the molecular weight of the products.

Ammonia treatment of the catalyst immediately after reduction or after a number of weeks of synthesis increased the activity and decreased the average molecular weight of the products. Hydrogenation of the nitrided catalysts caused a decrease in activity and increased the molecular weight of the products; however, when a nitrided catalyst that had been used in the synthesis for a number of weeks was hydrogenated, the activity of the resulting catalyst was greater than that of a corresponding reduced catalyst that had not been nitrided. Possibly the increased activity of these reduced-nitrided catalysts is due to carbidic carbon remaining in the catalyst after hydrogenation. Nitrides are gradually converted to carbonitrides in the course of the synthesis, and, on hydrogenation, some of the carbon may remain as carbide. It has been shown that iron carbides are difficult to reduce.

Catalysts converted to ϵ-phase nitride show the greatest increase in activity. The ϵ-phase nitrides have the same crystal structure as hexagonal Fe_2C carbide, which has been found previously in most active iron Fischer-Tropsch catalysts. Possibly the arrangement and spacing of the iron atoms in the hexagonal carbide and the ϵ-phase nitrides cause the high activity of catalysts containing these bulk phases. In the synthesis, the nitrogen atoms in the surface layers of the catalyst probably can be replaced easily by carbon atoms, and the active surface actually may be a carbide. The resistance of nitrided catalysts to oxidation also may contribute to their increased activity and longer life.

Although it has now been established that carbides of iron are not intermediates in the synthesis, it is certain that iron catalysts containing fairly large amounts of carbides or nitrides usually are more active than similar hydrogen-reduced catalysts. The way that interstitial compounds of carbon and nitrogen act as substrates for active catalysts is not understood, but it may possibly be related to differences in the geometry of the resulting catalytic surfaces. This work with iron nitrides opens a new field in catalysts, which may be pursued by the introduction of other elements into the iron lattice.

Attempts were made to decrease the high yields of gaseous hydrocarbons associated with nitrided fused iron catalysts by decreasing the particle size of the catalyst. Studies in bench-scale catalyst-testing units showed that this is possible; a 40- to 60-mesh catalyst decreased the operating temperature from 238° to 219° C., with a resultant decrease in production of gaseous hydrocarbons. Indeed, the products obtained from the fine-mesh catalyst were very similar to those produced by a reduced, unnitrided catalyst operated at 258° C.

The effect of synthesis-gas composition upon the activity and selectivity of synthetic-ammonia-type catalyst was studied in laboratory-scale reactors in tests of long duration. In contrast to previous similar tests made over very short periods, the present results indicate a definite advantage in using a carbon monoxide-rich synthesis gas. The yields of methane and other gaseous hydrocarbons decreased with increasing $CO:H_2$ ratio; at the same time, the average molecular weight of the products increased. The differences in the results of these two groups of tests may possibly be attributed to a constant catalyst composition during the short tests and a changing catalyst composition during the long tests.

A study was made of the changes that occur in fused iron synthetic-ammonia-type catalysts during such treatments as reduction, oxidation, and nitriding. The results indicated that the pore volume produced during reduction is a result of a decrease in volume accompanying the transformation of magnetite to α-iron, whereas the external volume of the particle remains constant. As the temperature of the reduction was increased, the external volume and pore volume of the catalyst particle remained essentially constant, but the surface area decreased, whereas the pore diameter increased. During oxidation with water vapor, the catalyst particles did not change in macroscopic dimensions. Oxidation was rapid initially, but the rate decreased to a negligible value before the catalyst was completely oxidized; partly oxidized samples reduced at a greater rate than the initial unreduced samples. When a catalyst is converted to interstitial phases - for example, nitride and probably carbide - the interstitial atoms expand the framework of the pore system, with the result that volume of mercury displaced, pore volume, and average pore diameter are increased.

Catalyst-oil Slurry Process. - In the catalyst-oil slurry process, a powdered catalyst is suspended in an oil that is nonvolatile under operating conditions, and synthesis gas is bubbled up through this suspension. Three different systems were operated before the most suitable design was chosen on the basis of the highest reproducibility of results and a minimum of mechanical difficulties.

The first type of reactor employed a slurry, which was circulated by means of the gas-lift principle. In the second reactor design, the slurry was circulated by means of a mechanical pump. Experiments carried out in both of these systems, however, usually were interrupted prematurely by severe operating difficulties stemming from deposition and settling of the catalyst particles.

Because of the inherent mechanical difficulties encountered with these circulating-slurry units when using precipitated iron catalysts, a static-bed type of reactor was constructed that does not involve circulation outside of the reactor. Synthesis gas enters at the bottom through a conical distributor, and reactor oil is separated from the catalyst by a porous metal filter in the upper section.

Work involving the catalyst-oil slurry process centered around the operation of static-bed slurry units, which do not utilize circulation outside of the reactor. Initial work with precipitated iron catalysts demonstrated that a circulating-slurry system was not a prerequisite for prolonged catalyst activity, and, hence, satisfactory studies could be made in bench-scale units in which heat removal is not a serious problem and without the mechanical difficulties that accompany slurry circulation. Parallel experiments performed in this bench-scale equipment showed that the results could be duplicated, and these units were used, therefore, to evaluate catalysts and to compare operating procedures.

Catalyst development for the slurry process has included (1) the study of methods of pretreating precipitated iron catalysts and of maintaining their activities, and (2) the search for other materials - such as synthetic-ammonia-type and ignited-iron-nitrate catalysts - which would be suitable for slurry operation. Typical of the results when precipitated iron catalysts were used were those obtained during a 238-hour period when a total oil yield of 125 grams per cubic meter of feed gas and a yield of hydrocarbon gases of 7.7 grams per cubic meter of feed gas were observed. These data represent a distribution of 48 percent and 3 percent, respectively, of the carbon monoxide that reacted. Pretreatment of an ignited-nitrate "fluff-type" iron catalyst in a manner similar to that normally afforded precipitated iron catalysts did not produce a sufficiently active catalyst. On the other hand, experiments with a very high concentration of fine (less than 250-mesh) synthetic-ammonia-type catalyst (1,045 grams of catalyst per liter of slurry) in a mineral-oil suspension indicated that a synthetic-ammonia-type catalyst can be satisfactorily

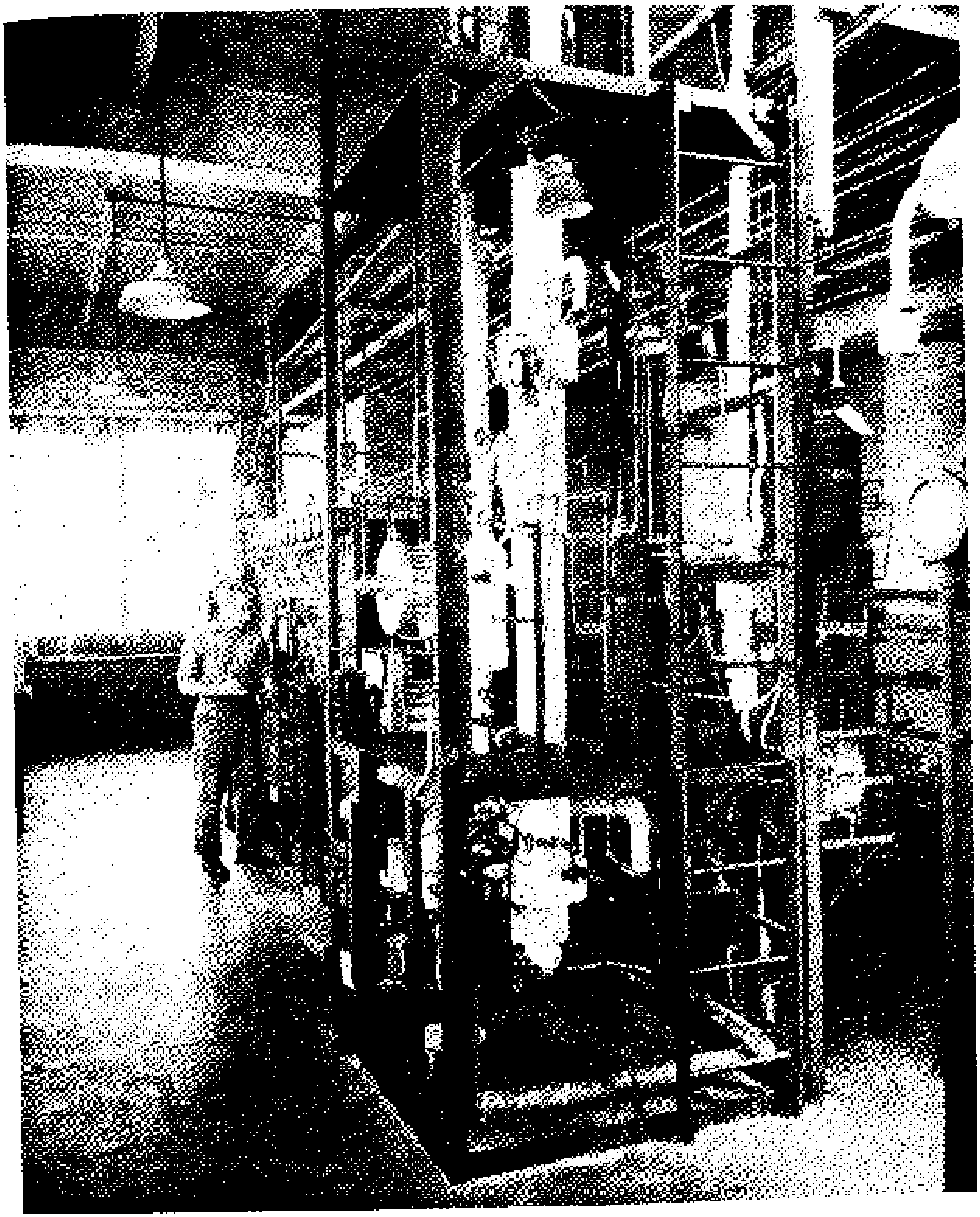

Figure 31. - Large catalyst-oil slurry unit.

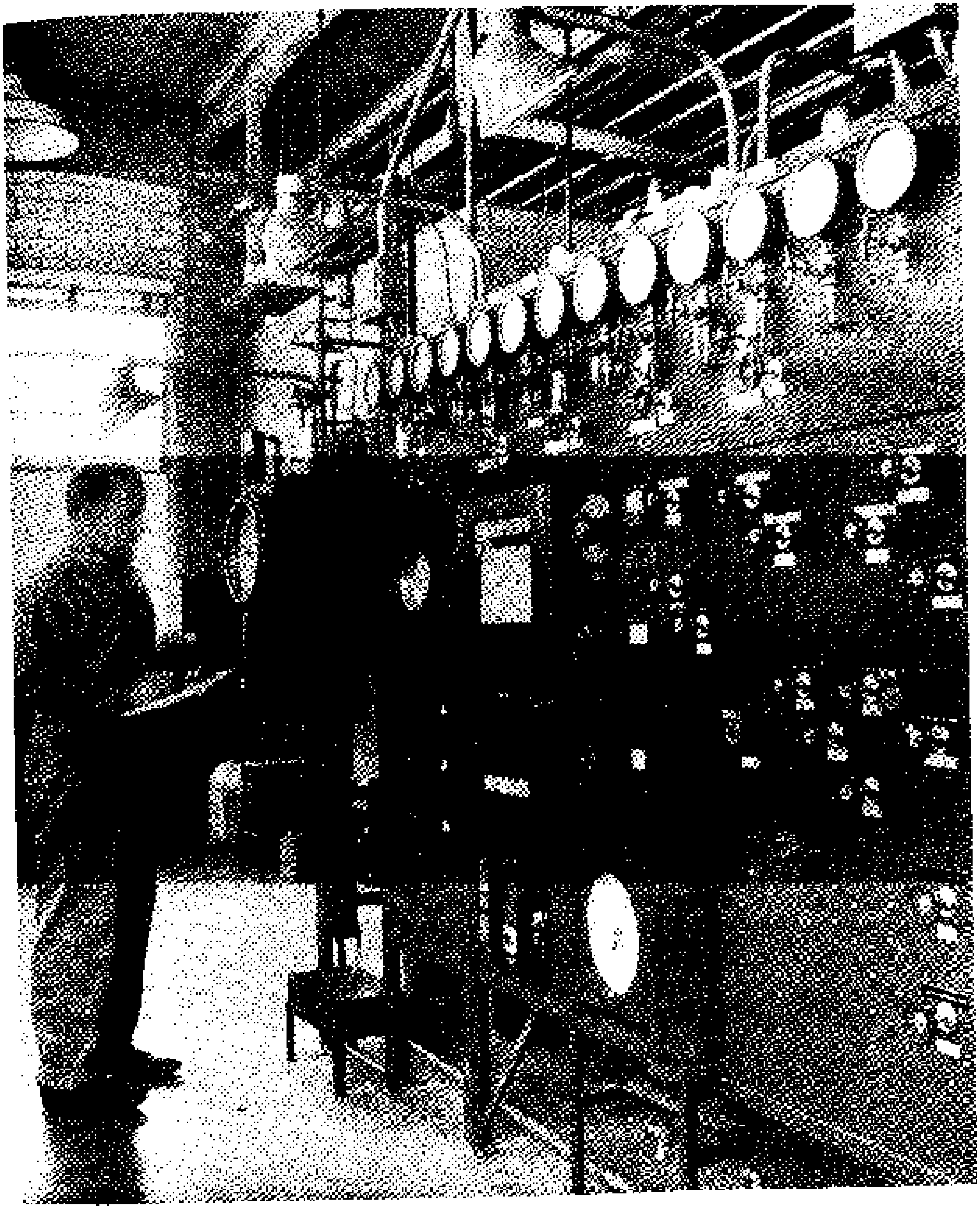

Figure 32. - Control panel for large catalyst-oil slurry unit.

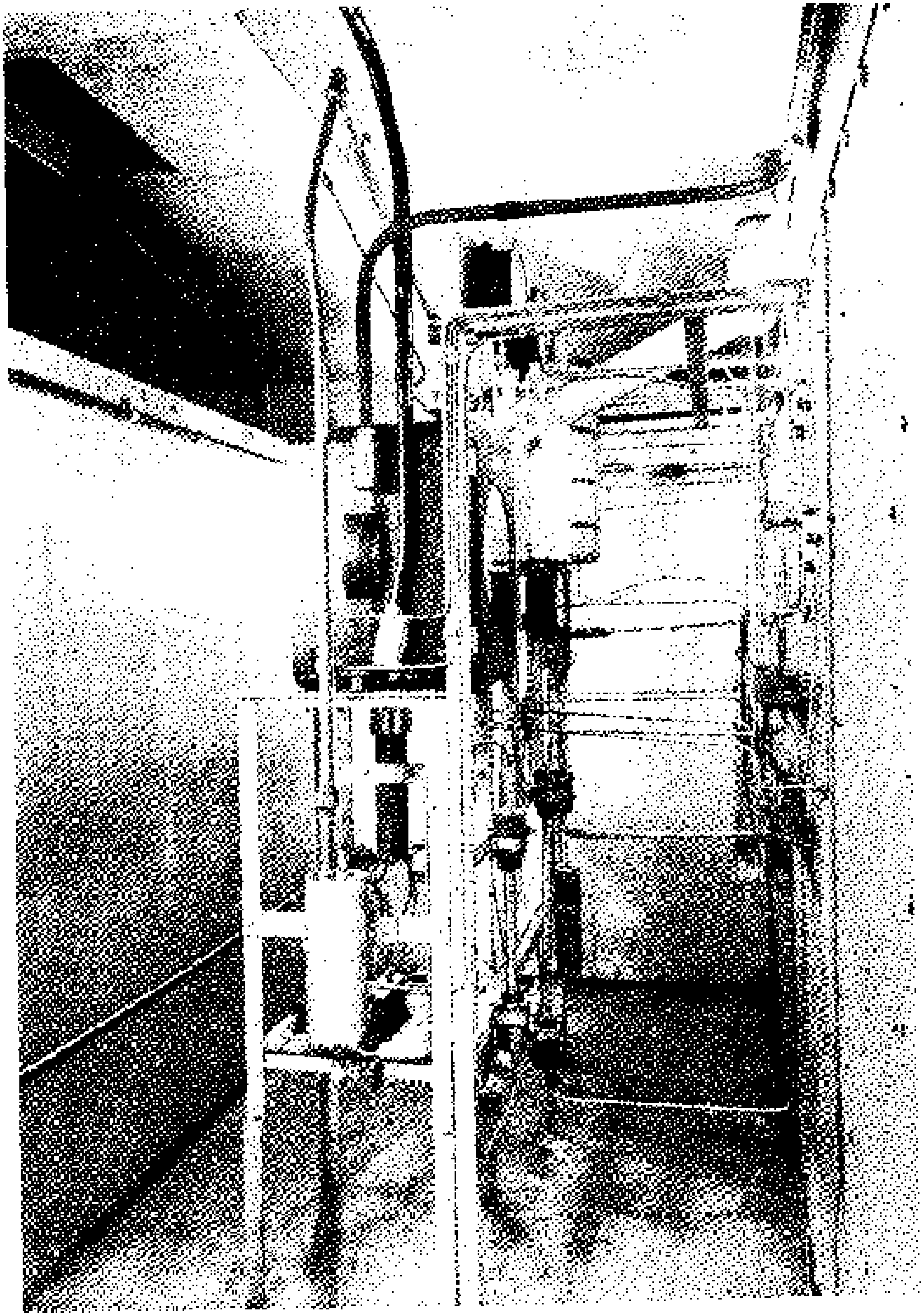

Figure 33. - High-pressure Fischer-Tropsch unit.

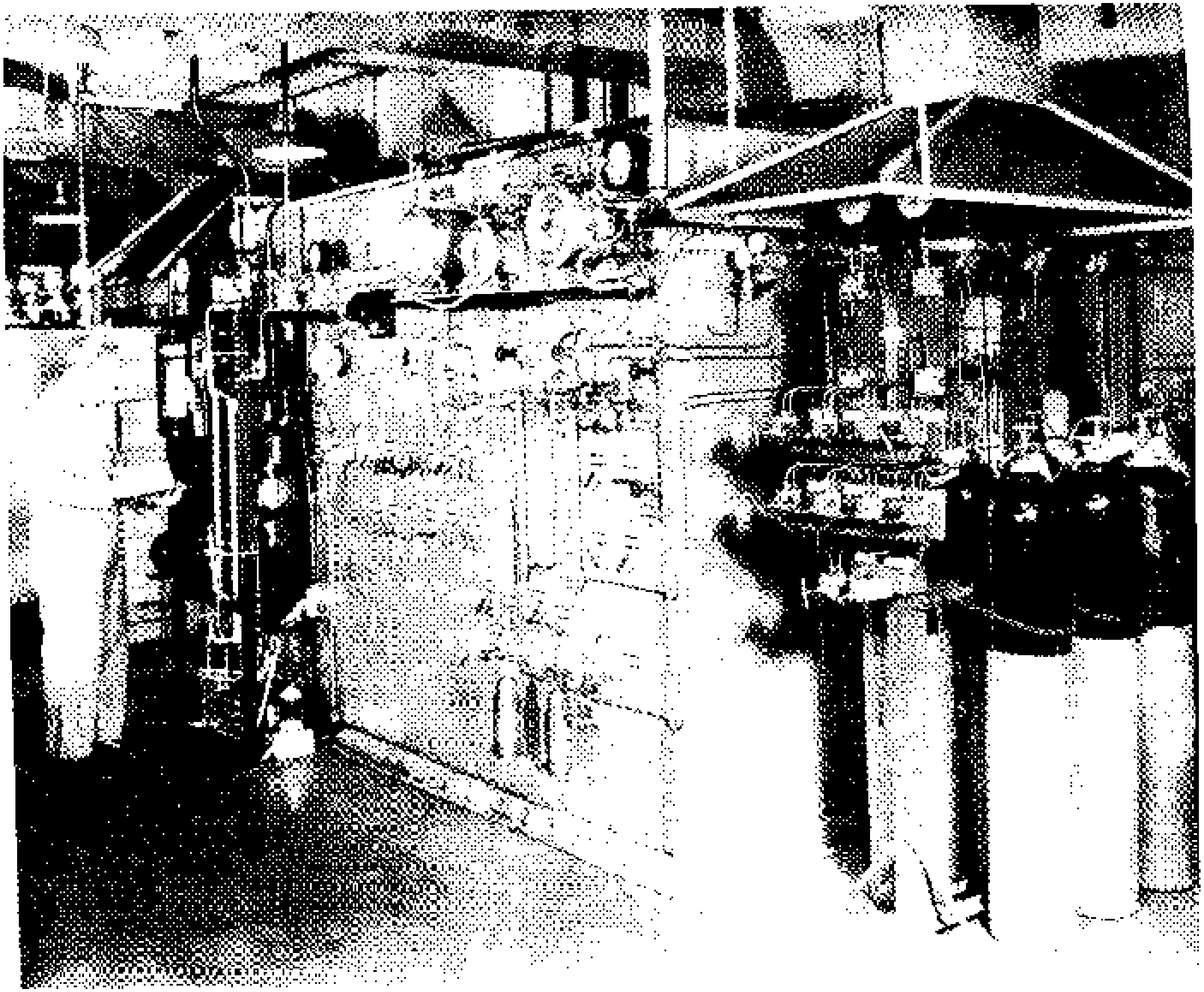

Figure 34. - Control panel for high-pressure Fischer-Tropsch unit.

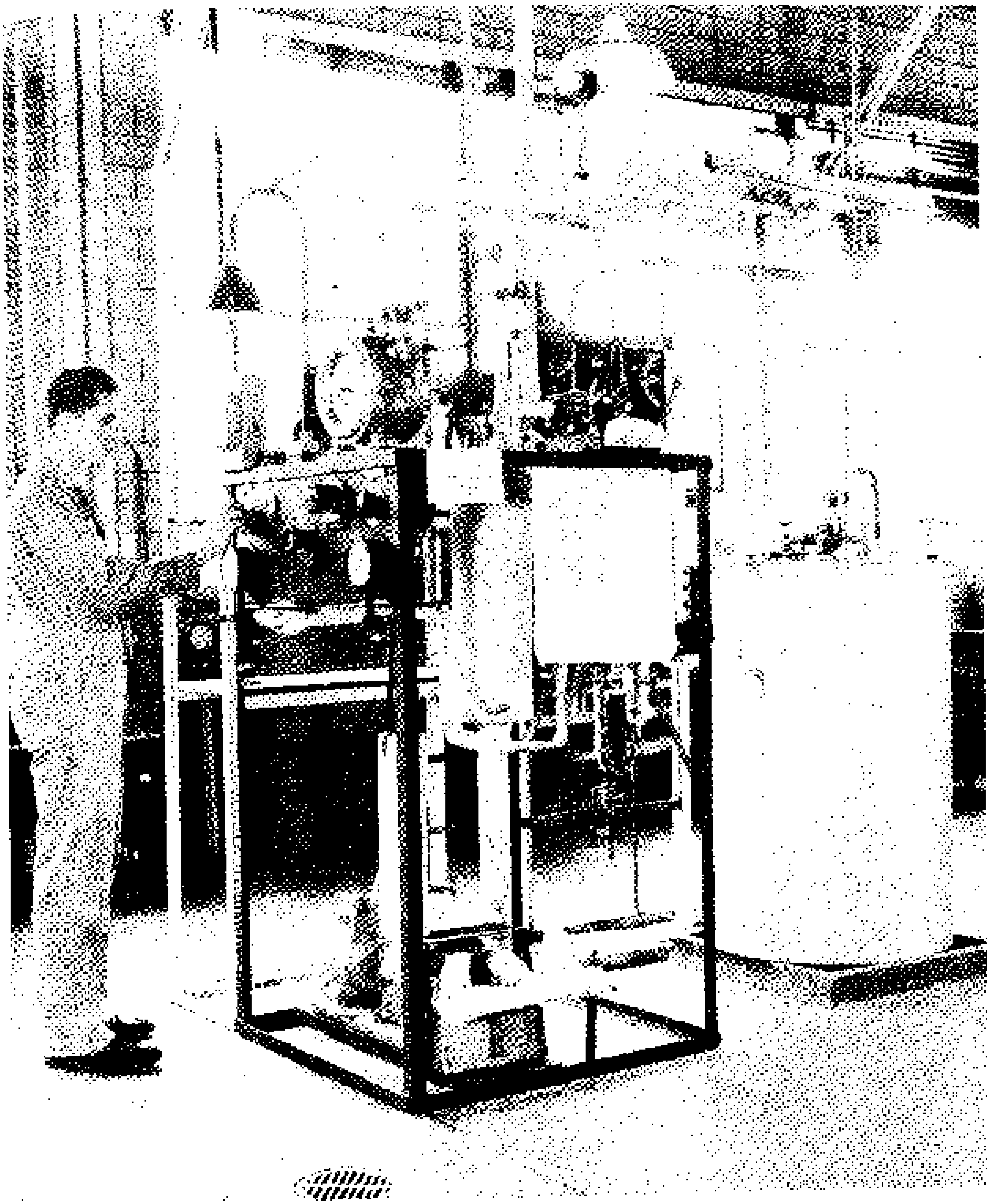

Figure 35. - Thermal-cracking unit.

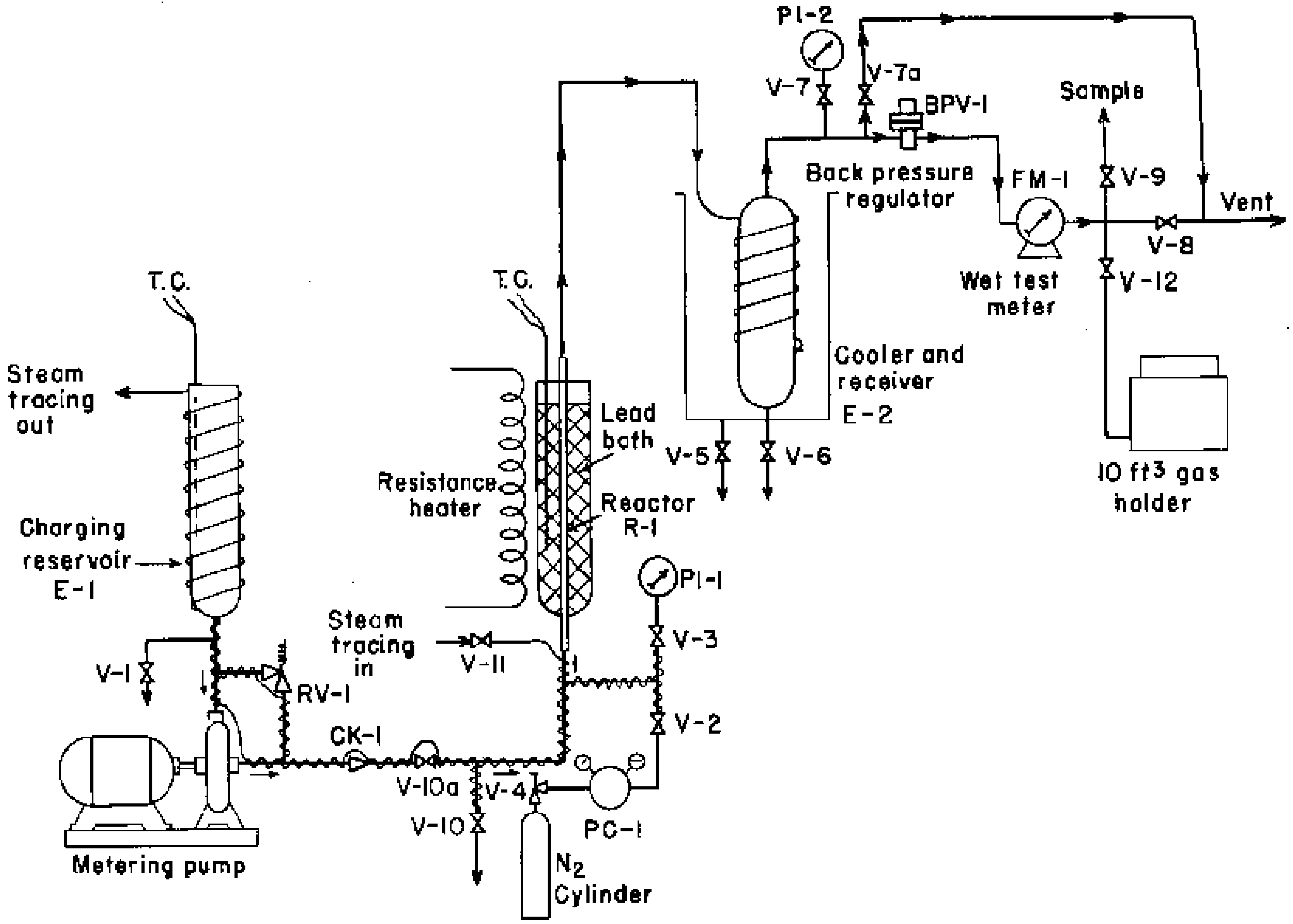

Figure 36. - Flow diagram of thermal cracking unit.

reduced and employed for the synthesis of hydrocarbons in a slurry system, but that settling of dense catalyst particles is a problem in small single-pass units, where low linear velocities are used.

The studies of process variations and operating procedures pointed up the necessity of rigid temperature control during the critical period when the catalyst is approaching the desired activity. Pressure-activation treatment of precipitated catalyst (300 p.s.i.) resulted in high wax accumulation in the reactor. Induction at 50 p.s.i. was found to be inadequate, but induction at 75 p.s.i. produced the desired conversion at 230° C. The use of carbon monoxide-rich synthesis gas during the induction period appears to accelerate the induction process while still producing a catalyst of high activity. Increasing the concentration of precipitated iron catalyst to 500 instead of the usual 300 grams per liter of slurry produced the desired conversion at about 202° C.

A large catalyst-oil slurry reactor (see figs. 31 and 32) of 13.5 liters capacity was operated with precipitated iron catalyst at a concentration of 500 grams per liter. The catalyst was pretreated in the reactor with resultant complete carbiding. After 400 hours on stream, when operations were suspended for alterations to the equipment, the operating temperature decreased from 235° to 216° C. for a 65-percent CO_2-free contraction, and 136 grams of C_3+ and 13 grams of C_1+C_2 hydrocarbons were obtained per cubic meter of fresh feed gas.

<u>High-pressure fixed-bed experiments</u>. - Construction of a continuous fixed-bed unit designed to operate at pressures up to 5,000 p.s.i. has been completed (see figs. 33 and 34). This unit will be used primarily to investigate the effects of pressure on reaction rate and product distribution. An orienting series of experiments with nitrided fused-iron catalysts is in progress.

<u>Thermal cracking of high-molecular-weight products</u>. - An experimental unit (figs. 35 and 36) was constructed to produce gasoline by thermal-cracking Diesel oil, fuel oil, and wax products produced in the internally cooled converter. The results of orienting experiments in the thermal-cracking unit indicate that the optimum conditions for cracking a Diesel-oil feedstock to products with a high gasoline-to-hydrocarbon gas ratio are 600° C., 200 p.s.i.g., and a space velocity of 12.4 volumes of oil per hour per volume of converter.

Reaction Mechanism Studies

The Oxo Reaction: Homologation of Alcohols

The production of aldehydes, ketones, and alcohols by the addition of carbon monoxide and hydrogen to olefins (the "OXO" reaction) is known to occur to some extent during the synthesis of hydrocarbons and oxygenated compounds by the Fischer-Tropsch process. As the homologation reaction has important implications in the mechanism of the Fischer-Tropsch process, considerable effort has been expended during the past year in studying the mechanism of the homologation itself. At 3,000 p.s.i. with equal parts of hydrogen and carbon monoxide and at 150° to 180° C., aliphatic olefins and alcohols react to form the alcohol with one more carbon atom. If the reaction is conducted at lower partial pressures, the aldehyde with one more carbon atom can easily be isolated as the major product. Thus, for example, when octene-1 was treated with synthesis gas at 875 p.s.i. initial pressure, a mixture of nonyl aldehydes and unchanged octene was obtained. Under essentially the same conditions, but at 3,000 p.s.i., a mixture of nonyl alcohols was obtained virtually free of aldehydes.