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

During the calendar year 1950, the laboratories and pilot plants at Bruceton, Pa., continued their attack on several fronts toward the development of new or improved processes for the production of liquid fuels from coal: The synthesis of liquid fuels from the gasification products of coal (Fischer-Tropsch and related processes), improvements in the direct high-pressure (3,000-10,000 p.s.i.) hydrogenation of coal (Bergius process), and the development of a medium-pressure (about 1,000 p.s.i.) fluidized coal-hydrogenation process.

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

Process Development

Pilot-plant Operations

Fischer-Tropsch operations in the pilot-plant stage at the Coal-to-Oil Laboratories of the Bureau of Mines have been carried out by use of an oil-circulation process with a submerged catalyst bed. Such a system permits the use of a simple reactor with no internal cooling surface and provides direct control of the catalyst temperature, eliminating the possibility of developing hot spots in the converter, which would result in the deposition of carbon and the deterioration of catalyst.

In operations with a fixed bed of catalyst, fresh feed and recycle gas enter the bottom of the converter and flow upward concurrently with the circulating oil. As the gas passes over the catalyst, reaction occurs, and heat is transferred to the cooling oil. An overflow pipe connected with the converter at a point above the catalyst bed conducts the exit gas and oil to a separating tank, from which the gases and vapors pass overhead to a condenser and recovery system; the cooling oil is returned to the reactor by a circulating pump.

Fixed-bed operation of the internally cooled converter has always been complicated by eventual cementing of the catalyst particles, and several changes in the operation of the system were made in an attempt to prevent this difficulty. A significant improvement occurred when the hydrogen:carbon monoxide ratio in the feed gas was increased. With a 1.3:1 ratio, it was possible to reduce the rate of catalyst cementation until a useful catalyst life of 4 to 5 months could be obtained. However, it was still quite difficult to remove the catalyst at the end of the experiment.

To eliminate the cementation problem, a new method of operation, the "moving catalyst bed," was developed. Smaller catalyst particles, i.e., 10- to 40-mesh instead of 6- to 10-mesh, were charged to the converter for moving-bed operation, and the linear velocity of the cooling oil was increased to such a degree that the catalyst bed expanded until the bed height was about 25 to 35 percent greater than its settled height. Considerable motion of the individual particles resulted from the high rate of oil circulation. A moving bed of synthetic-ammonia-type catalyst was operated successfully in this manner for several months without increase in the pressure drop across the catalyst and entirely without cementation of the bed. Although some attrition of the catalyst occurred, even after 4 months of operation this had little or no effect upon the activity, and the catalyst carry-over from the converter to the oil-circulating lines was negligible. These and other advantages of the moving bed as compared to the fixed bed are shown in table 9 and include:

1. Greater catalyst economy. - The use of smaller catalyst particles with greater geometric surface area per unit weight resulted in greater conversion per pound of catalyst at the same conditions of synthesis.

2. Lower operating temperatures are possible for the same amount of conversio

3. Charging or withdrawing catalyst was facilitated both during operation and upon termination of the run.

4. A greater space-time yield, based on converter volume as well as catalyst volume, is obtained.

TABLE 9. - Comparison of operating conditions in oil-submerged fixed and moving beds (300 p.s.i.g. operation)

Experiment number	14	22
Catalyst bed	Fixed bed, 8 ft., 4-6 mesh	Moving, 4 ft. static height, 5 ft. expanded, 6-20 mesh
Weight of iron charged, lb.	42.8	23.5
Ratio of H_2:CO in feed gas	1:1	1:1
Total catalyst age, hr.	2,300	2,355
Temperature, maximum, °C.	254-265	240-250
Temperature differential, °C.	16	6
Pressure drop across bed, p.s.i.:		
Start of experiment	4	5
End of experiment	49	5
Feed gas rate, SCFH	174	
Space velocity, STP (vol. x vol.$^{-1}$ x hr.$^{-1}$)	300	600
Recycle ratio (tail gas:fresh gas)	2.0:1	1.0:1
Conversion:		
CO, percent	69.9	70.7
H_2, percent	69.9	68.5
H_2 + CO, percent	69.9	69.5
Usage ratio	1.0	0.95
Space-weight conversion (cu. ft. H_2 + CO converted per hr. per lb. Fe)	2.01	3.56

On the basis of the many improvements introduced by the moving-bed system, fixed-bed experiments were terminated, and further studies were directed toward investigating operating and yield data for the moving-bed type of operation.

In the course of normal operations, the appearance of erratic results, such as abnormally high production of gaseous hydrocarbons and low synthesis gas conversion immediately following reduction of the catalyst, was traced to the presence of large amounts of sulfur in the synthesis gas. The origin of the contamination was located finally in the water of the gasholders. Although no definite cause for the contamination could be established, existing evidence suggests that the sulfide was produced by the action of bacteria on the sulfates present in the Bruceton water supply. Precipitation of the sulfur as cupric sulfide and maintenance of a proper hydrogen-ion concentration in the gasholder water restored the synthesis-gas supply to the

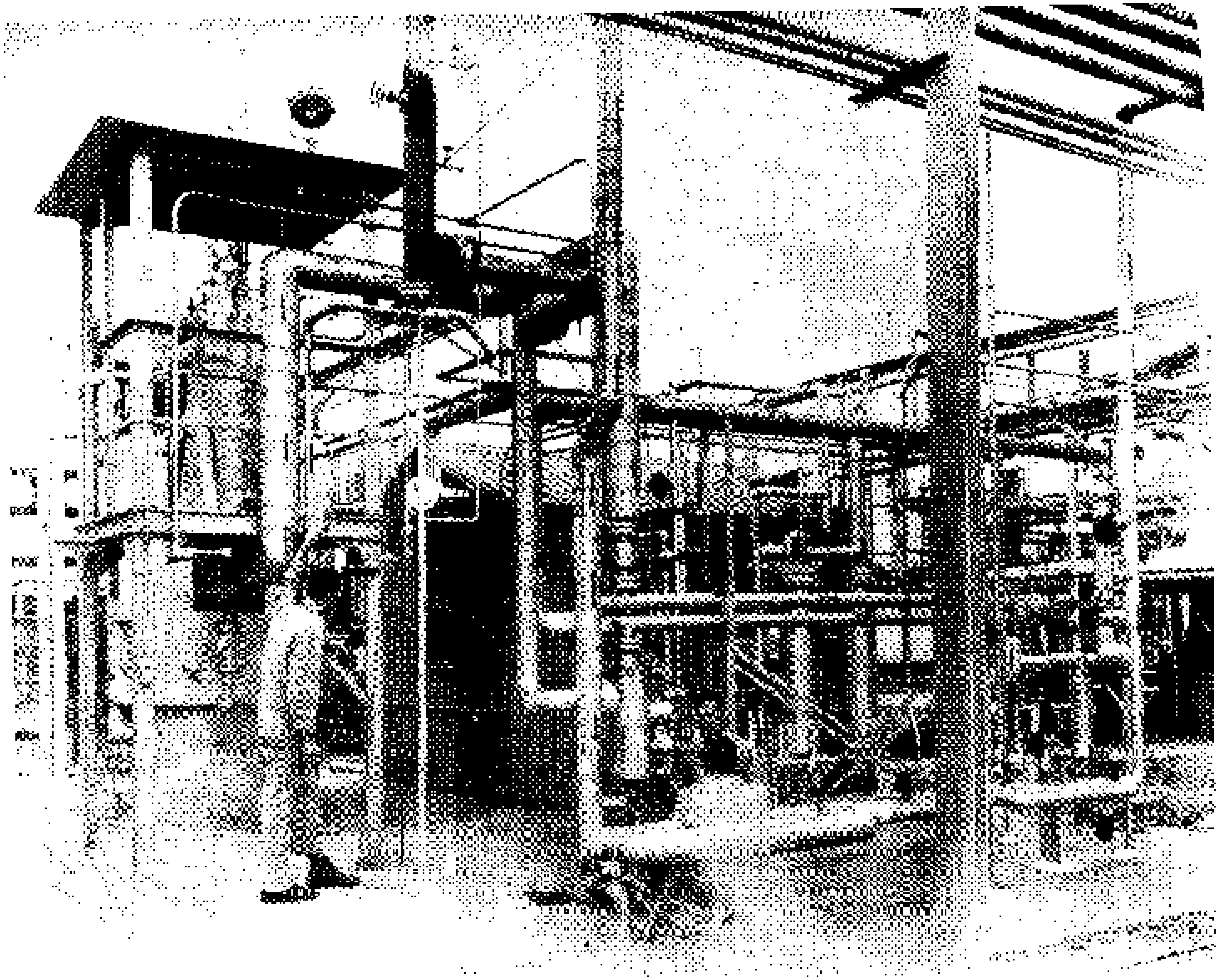

Figure 27. - Catalyst reduction unit.

required purity and provided means for controlling this source of sulfur contamination in subsequent operations.

Using a synthetic-ammonia-type catalyst, the internally cooled converter was operated with a carbon monoxide-rich synthesis gas having an H_2:CO ratio of 0.7:1. The results indicated that the use of a feed gas of this composition required higher operating temperatures (270° C.) to produce the desired conversion, but that even at these higher temperatures the yields of gaseous hydrocarbons were smaller than when 1 H_2:1 CO feed gas was used. In addition, by this use of carbon monoxide-rich feed gas, an H_2:CO usage ratio equal to the H_2:CO ratio of the feed gas could be attained without exceeding a gas-recycle ratio of 1:1.

Operation of a stripping column in an arrangement that simulated actual series operation with the internally cooled converter using 1 H_2:1 CO feed gas resulted in separation of the water otherwise dissolved in the circulating oil. This, in turn, increased the H_2:CO usage ratio by retarding the water-gas shift reaction, $H_2O + CO = H_2 + CO_2$. Usage ratios of 0.94 to 0.99 were obtained by installing a potassium carbonate scrubber in the system to reduce the carbon dioxide content of the recycle gas. With this arrangement in gas-recycle operation, a synthesis-gas conversion of 90 percent could be obtained in one pass by raising the operating temperature 10 degrees above normal (to 260° C.). Without removal of carbon dioxide from the recycle gas, no more than 85 percent synthesis gas conversion could be obtained in a single stage even at temperatures up to 295° C. and at higher gas-recycle rates.

In view of the improved results obtained by scrubbing out the carbon dioxide from the recycle gas with potassium carbonate solution when 1 H_2:1 CO synthesis gas was used, a similar procedure was incorporated into operation with 0.7 H_2:1 CO synthesis gas. At a constant operating temperature of 269° C., it was possible to increase the synthesis-gas conversion from 67 to 76 percent in this way. The results obtained thus far, however, have shown that, in operations with carbon monoxide-rich feed gas and high conversions, the magnesia-promoted synthetic-ammonia-type catalysts have only a relatively short life. In laboratory tests, the nitrided, alumina-promoted, synthetic-ammonia-type catalyst has shown much higher activity and durability with carbon monoxide-rich feed gas. Pilot plant tests with this catalyst are scheduled for the near future.

As a means of removing the oxygenated compounds from the overhead vapors produced by operating the internally cooled converter with synthetic-ammonia-type catalyst, these vapors were treated with bauxite in situ. Comparison of Cyclocel and Alumina F-1 bauxites showed that at 300° and 365° C., respectively, both catalysts were active in removing the oxygenated compounds from the oil stream (about 80 percent). Removal of oxygenated compounds from the water layer, however, was not as pronounced, and in this case the Alumina F-1 treatment was more effective than the Cyclocel, although the use of Cyclocel at a higher temperature would be expected to bring about more complete removal. Virtually no shifting of the double bonds was effected by the Alumina catalyst, but use of Cyclocel catalyst exerted a most pronounced effect in this direction.

The catalyst-reduction unit (see fig. 27) designed for the preparation of catalyst for the barrel-a-day Fischer-Tropsch pilot plant has been completed and tested under the anticipated operating conditions (250 p.s.i. in the driers and atmospheric pressure in the reductor; operating temperature, 300° C.). As a result of these preliminary tests, minor modifications in design of equipment are being made.

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.

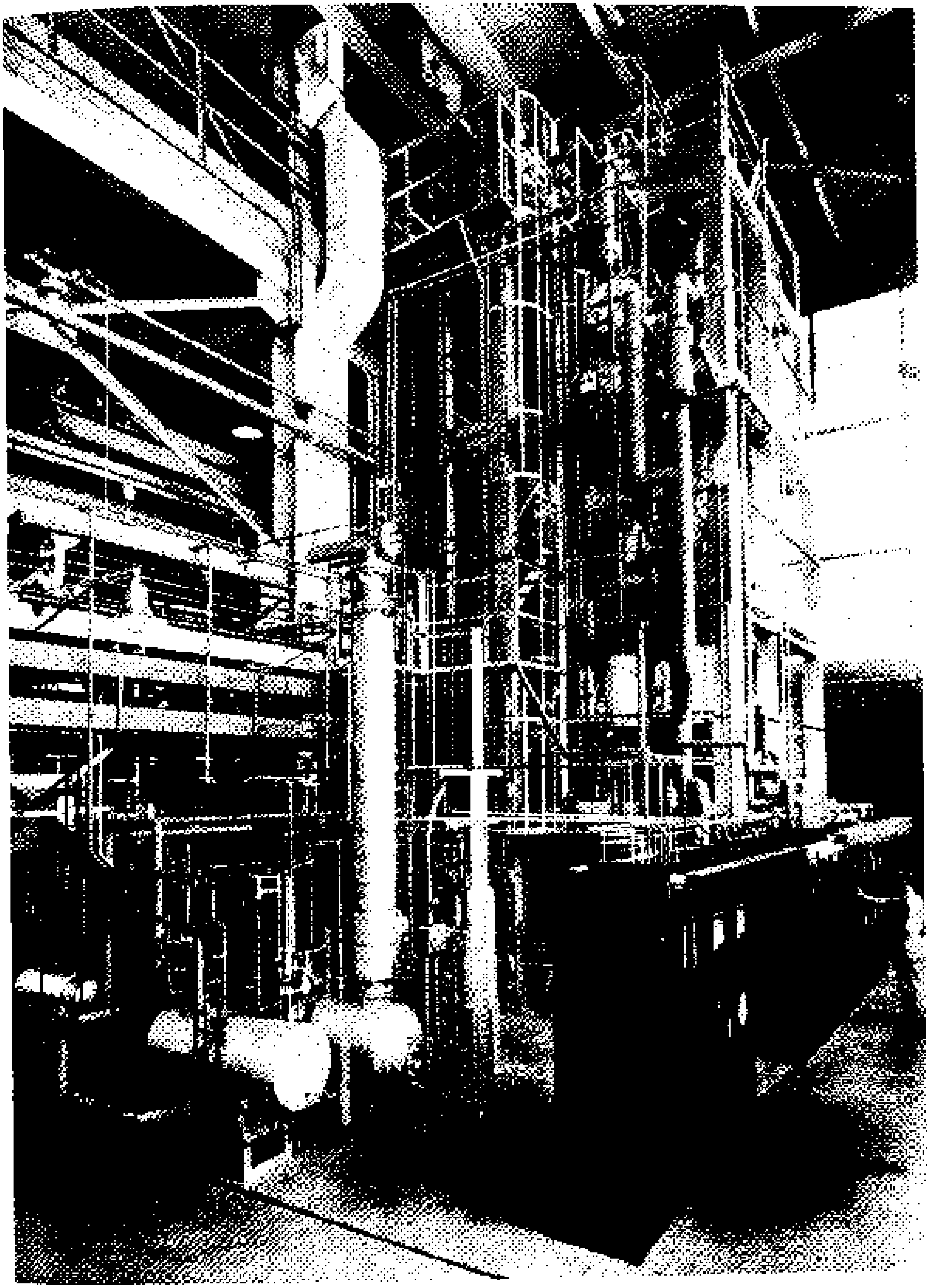

Figure 28. - Barrel-a-day Fischer-Tropsch pilot plant.

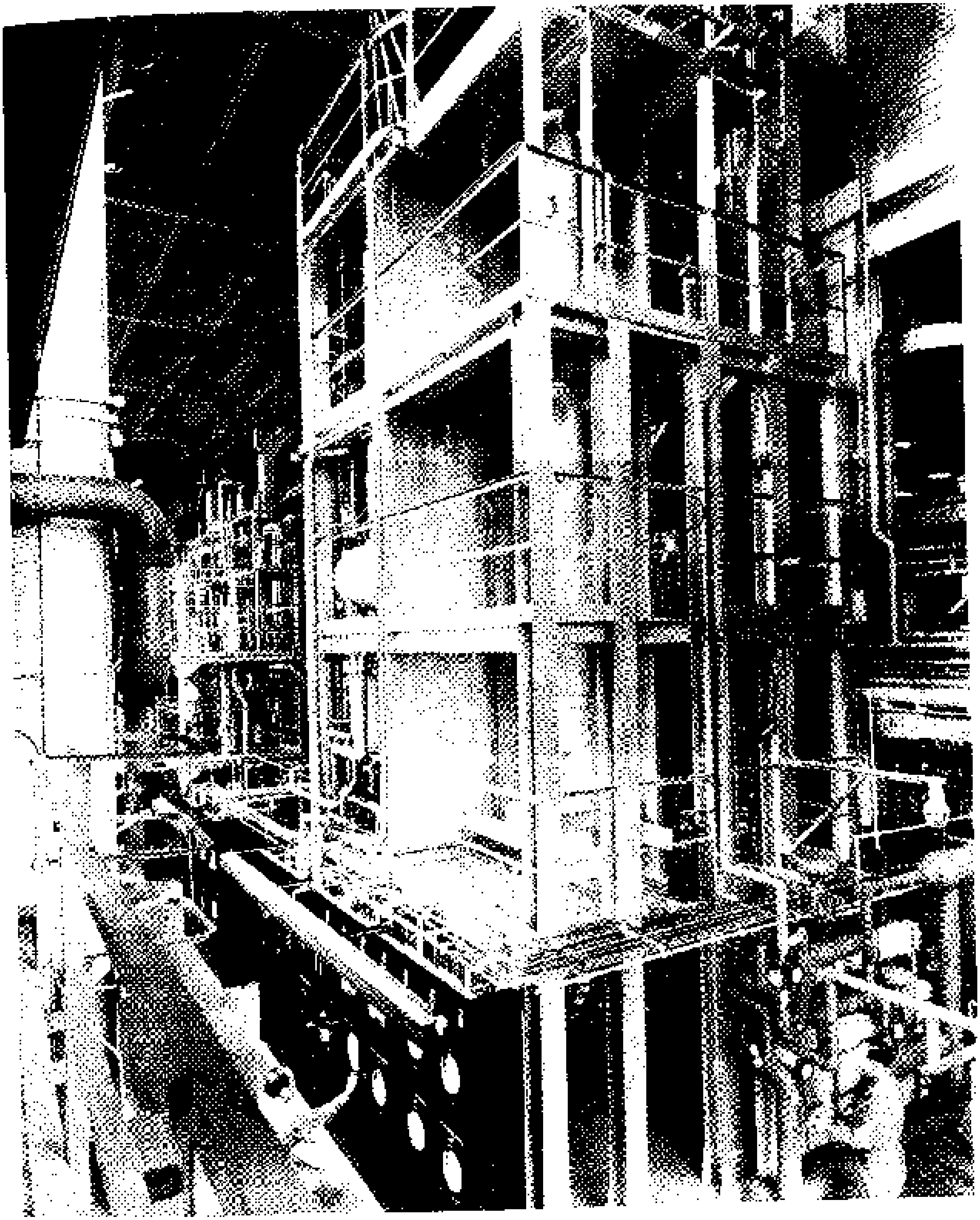

Figure 29. - Barrel-a-day Fischer-Tropsch pilot plant.

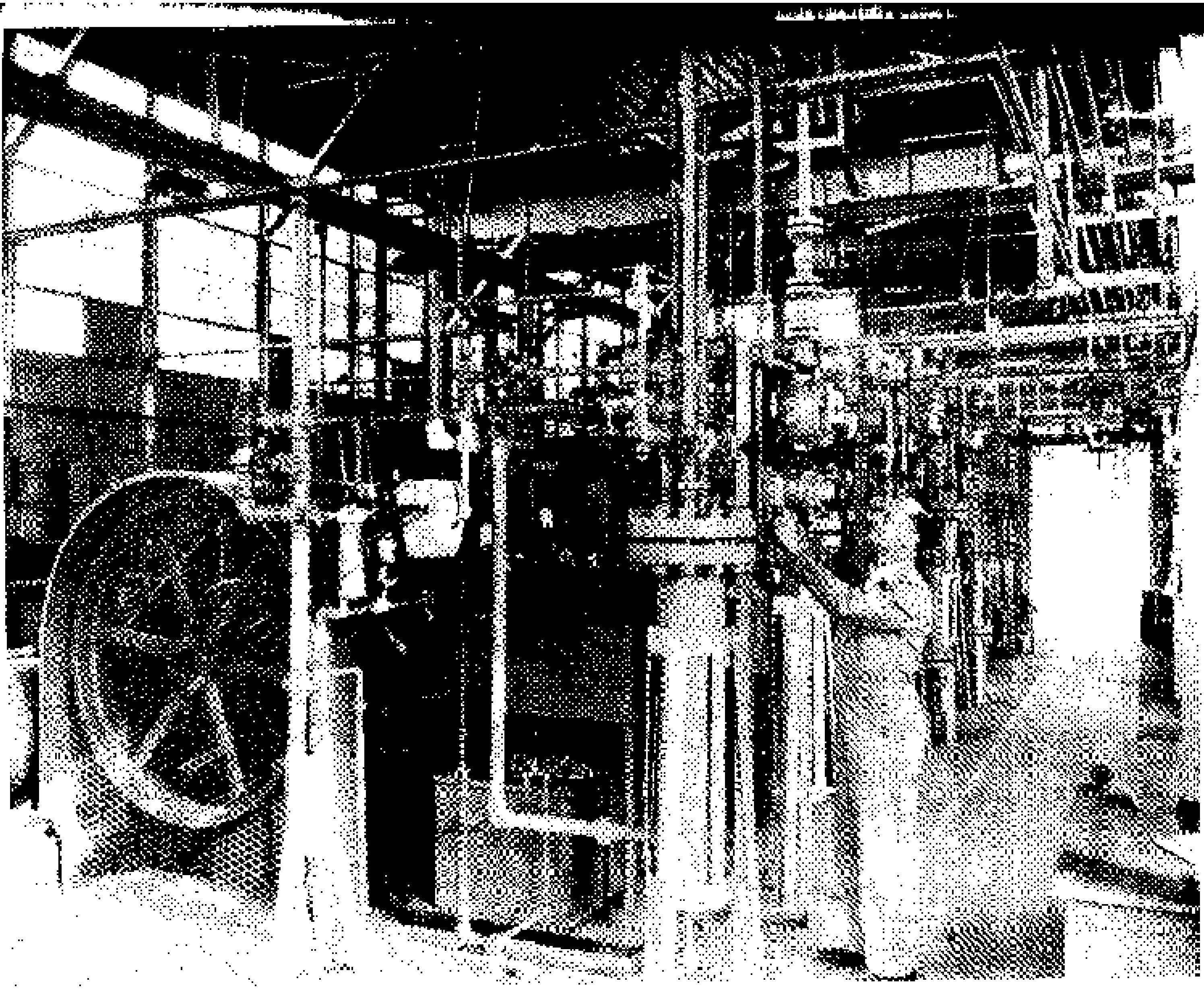

Figure 30. - Compressor house.