

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

Work at the Bruceton, Pa., laboratories and pilot plants on the synthesis of liquid fuels from gasified coal included development of an exceptionally sturdy and long-lived Fischer-Tropsch catalyst, of an economical process for the removal of carbon dioxide from synthesis gas, and of a commercially feasible synthesis of alcohols. Of particular importance in coal hydrogenation were autoclave assays of a number of coals, a new method for predicting the product yield from residual oil, and development of the first American catalyst for vapor-phase hydrogenation.

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

Process Development

Pilot-Plant Operations

Synthesis Experiments

In pilot-plant operation of the so-called oil-circulation Fischer-Tropsch process, synthesis gas - a mixture of carbon monoxide and hydrogen - is carried upward through the catalyst concurrently with circulating oil. The heat of the exothermic reaction is transferred to this cooling oil, so that no internal cooling surfaces are needed. When necessary the oil is pumped at a high enough rate to expand the catalyst bed about 5 percent, causing slight movement of the catalyst particles and preventing their cementation into a solid mass.

Until now, a major cause of trouble has been disintegration of the catalyst. In the 1951 Annual Report, it was noted that an experiment had to be terminated after about 1,200 hours because over half of the catalyst had disintegrated and been carried out of the converter as fines in the cooling oil. A major portion of the work in 1952 therefore was devoted to possible solutions of this problem. After preliminary laboratory-scale tests had yielded promising results, pilot-plant tests were made with steel shot and iron lathe turnings.

A special activation procedure was employed with these catalysts, which consisted of massive, nonporous particles in contrast to the previously used fused catalyst, in which the promoters are incorporated during fusion and which become highly porous upon reduction. A special furnace was constructed in which the catalysts can be oxidized at up to 600° C. with steam. After oxidation the catalysts are promoted with alkali by immersion in a dilute solution of potassium carbonate. When dry they are reduced with hydrogen at about 400° C. The sulfur content of the catalysts is slightly reduced during this procedure (0.10 to 0.08 percent in one batch of steel shot), but the remaining sulfur appears to have no deleterious effect on the catalytic activity.

In one experiment about 47 pounds of 1/16-inch-diameter steel shot was operated with synthesis gas consisting of equal amounts of hydrogen and carbon monoxide. At first only about 30-percent contraction of the gas (a measure of the activity of the catalyst) was observed at 300° C. Also, the rate of flow of coolant oil was low so that cementation of the catalyst became quite noticeable after 550 hours. Reactivation by reduction only was ineffective; however, repetition of the original activating operations (oxidation, impregnation, reduction) resulted in twice as much oxidation of the catalyst compared with initial activation and in a correspondingly deeper active layer on the steel shot. As a result the activity increased so much that 70 percent of the gas could be converted at only about 250° C.

After 1,745 hours of continuous operation, during much of which the activity of the shot kept improving, a mechanical failure necessitated interruption of the experiment; however, the catalyst was in excellent physical condition. Synthesis was resumed after reactivation and continued until the activity became quite low after a total synthesis time exceeding 4,000 hours. This decline in activity may have been connected with rather unfavorable synthesis conditions - high wax content of cooling oil - that were purposely imposed on the catalyst. Reactivation was unsuccessful, and the experiment was discontinued after about 6 months of actual operation. Very little deterioration of the catalyst was noted; this was mechanically the most rugged and chemically the most durable catalyst tested thus far. Preliminary experiments to determine whether the shot may be reactivated (oxidized and reduced only) while immersed in oil in the synthesis reactor were not promising.

The 1/16-inch shot had excellent mechanical properties, but its activity was lower than that of 6- to 20-mesh reduced, fused-iron catalyst tested in the plant. This fact may be due to the difference in the geometric surface areas of the catalysts. To determine the effect of this area on activity, tests are now under way with 1/32-inch shot and with lathe turnings of low-carbon iron. Their activation proceeded in a similar manner, that is, oxidation, impregnation, and reduction. However, about four times as much oxidation and reduction took place on the lathe turnings as on steel shot. Synthesis with both catalysts was stopped after a few hundred hours to permit their reactivation, a procedure that resulted in a considerable increase of activity of the 1/16-inch shot.

One experiment was made with nitrided fused iron (synthetic-ammonia-type catalyst) in the pilot plant (see fig. 24). Because of the steadily declining yield of oxygenated compounds, the test was terminated after almost 1,000 hours. It is believed that a faulty preheater had a deleterious effect on the catalyst during nitriding. During most of the operation, 70 to 90 percent of the liquid and solid product was in the gasoline range, and less than 2 percent was wax.

Purification of Synthesis Gas

Economical removal of carbon dioxide from synthesis gas is very important for development of a commercially useful synthesis process. Carbon dioxide is not only a diluent but is also thought to be a catalyst poison when present in fairly large concentrations. About 160 cubic feet of this gas is manufactured with each 1,000 cubic feet of pure synthesis gas, and an equal amount is formed during synthesis.

Originally, dilute alkali carbonate solutions were used commercially for scrubbing carbon dioxide; more recently, ethanolamine has replaced these. Both types of solution require heat-exchange equipment, and evaporative losses of amine may become rather expensive. At elevated pressures, plain water may be used. However, pumping costs become high because of the large amounts of water required, and loss of desirable gas constituents by solution in the water may be noticeable.

In the most-promising process for making synthesis gas, coal, oxygen, and steam are reacted under pressures of 300 to 500 p.s.i.g. To take full advantage of the availability of impure gas at elevated temperature and pressure, a scrubbing process has been developed, using hot, concentrated potassium carbonate solutions. First, solubilities of concentrated mixtures of potassium carbonate and bicarbonate at high temperatures had to be determined. Equilibrium partial pressures of carbon dioxide in these solutions, over-all transfer coefficients (absorption per unit time, volume of reactor, and pressure differential), and absorptive capacities of the solutions for carbon dioxide were then measured, and the consumption of steam was determined.

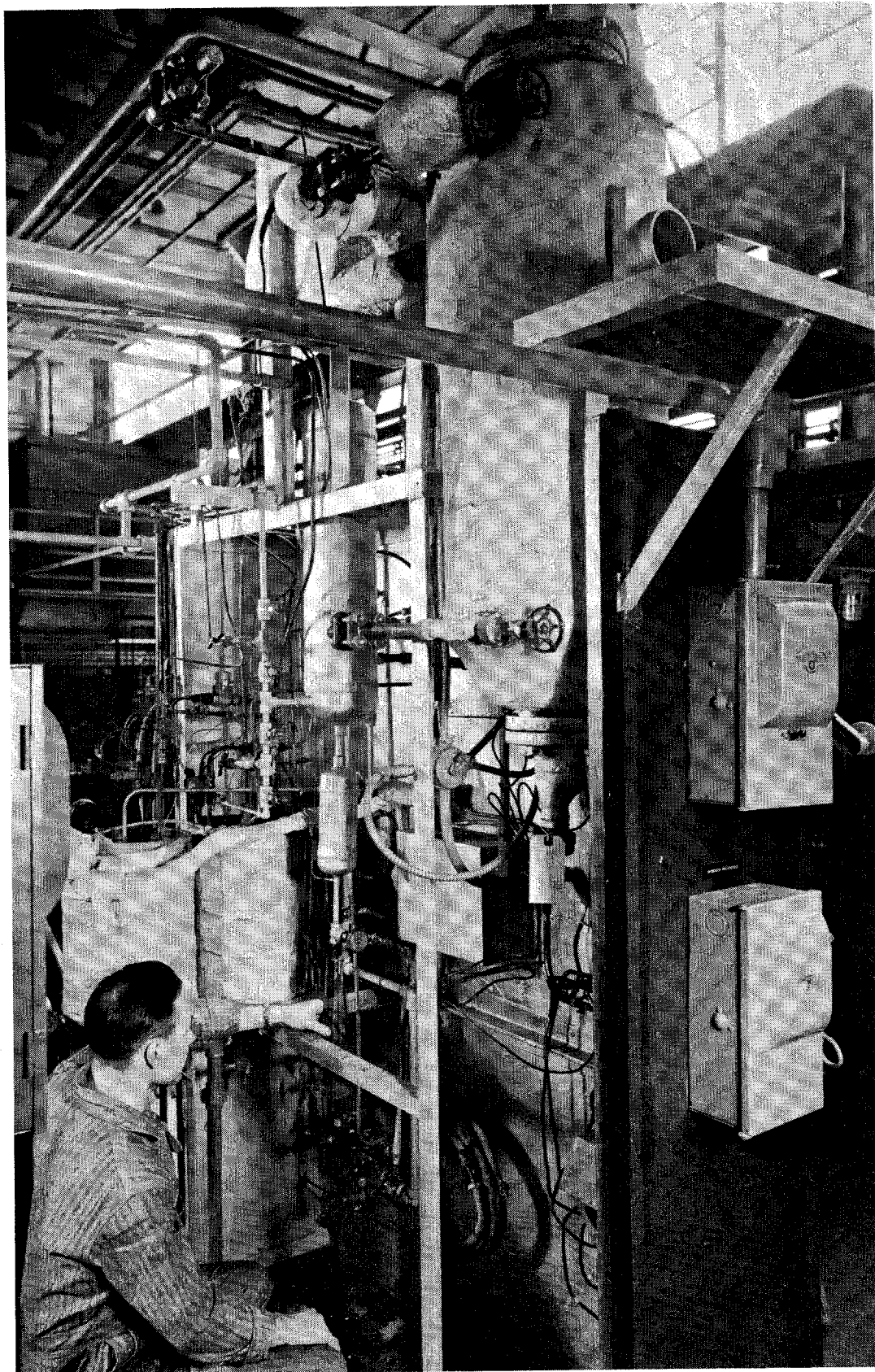


Figure 24. - Tilting furnace used in pilot plant for reducing and nitriding catalysts.

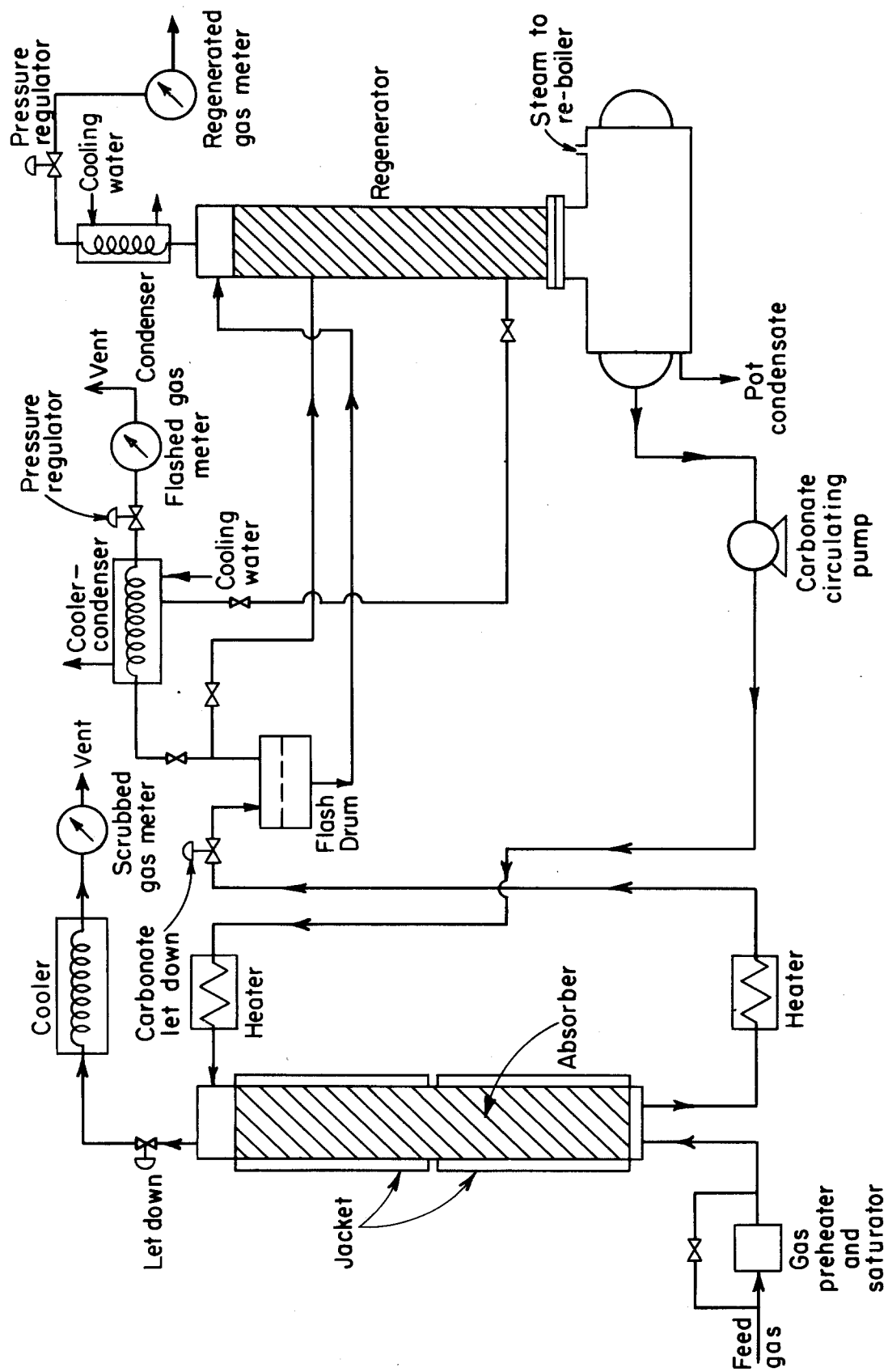


Figure 25. - Schematic diagram of pilot plant for hot carbonate scrubbing.

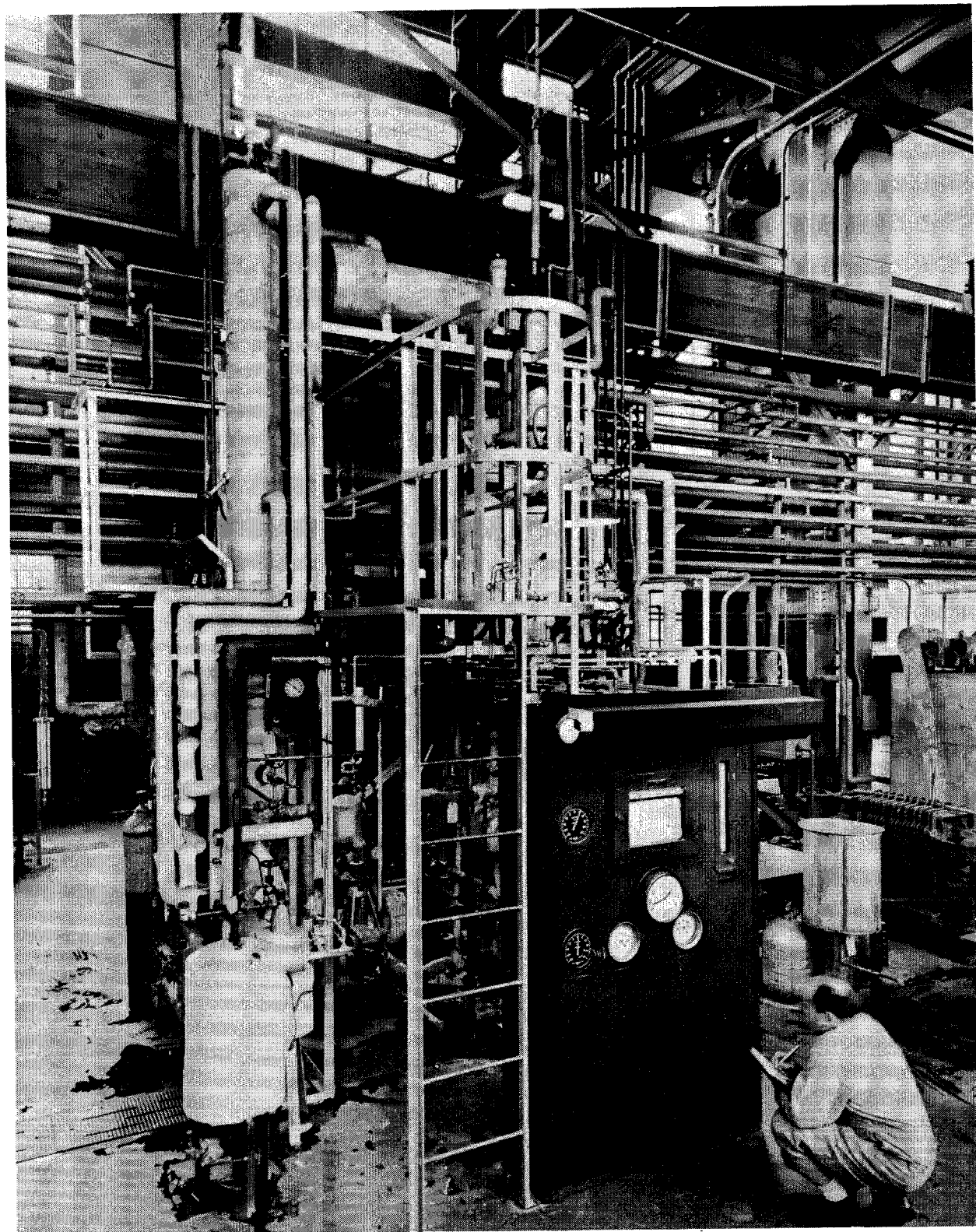


Figure 26. - Hot potassium carbonate scrubber for removing carbon dioxide from synthesis gas.

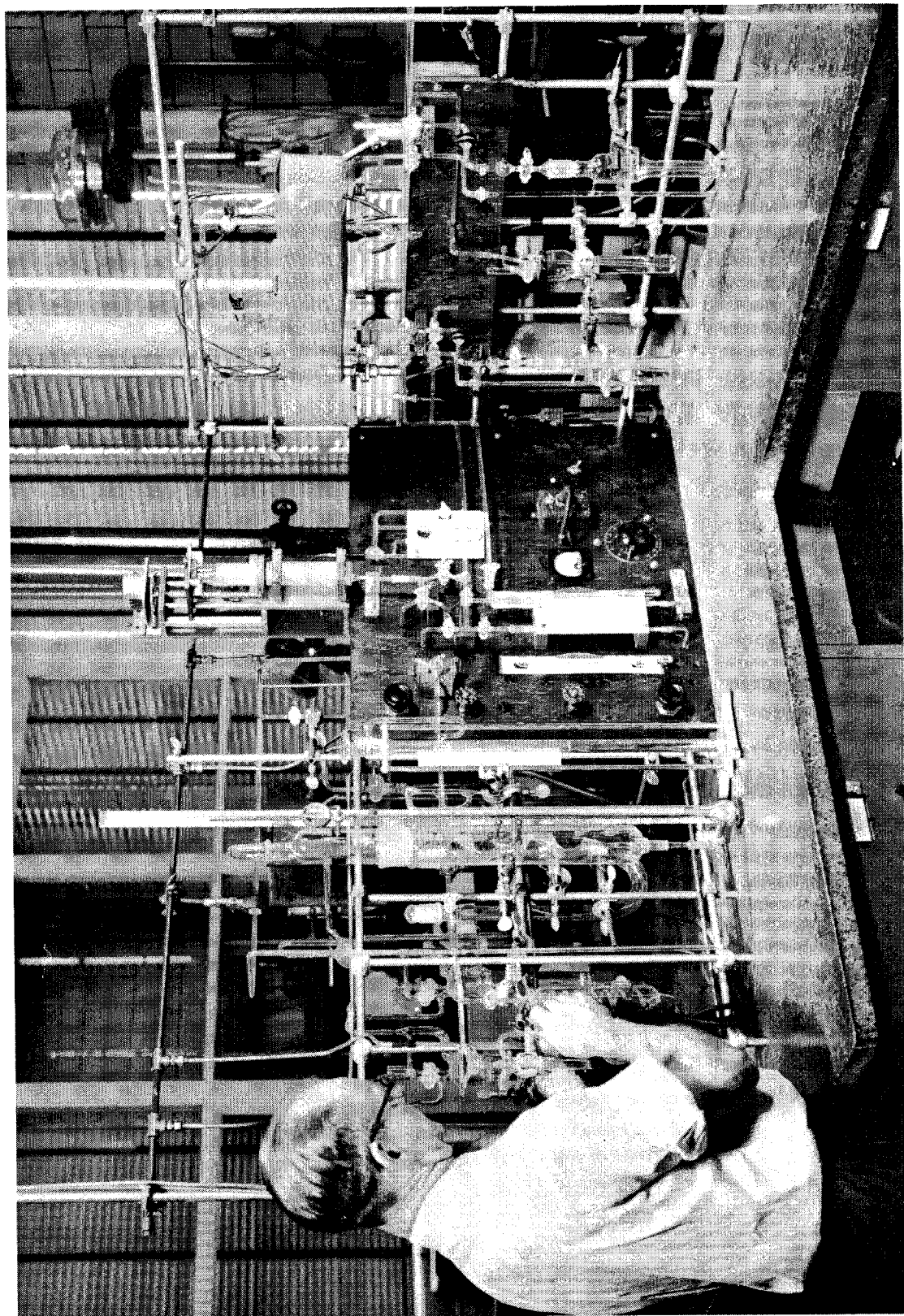


Figure 27. - Apparatus for sulfur analysis.

A schematic diagram of the pilot plant is given in figure 25; the actual plant is shown in figure 26. The scrubbing solution takes up carbon dioxide in the absorber, is flashed and thus partly regenerated in the flash drum, and is steam-stripped and fully regenerated in the regenerator, whence it returns to the absorber.

The results of pilot-plant runs indicate that this procedure is better than conventional scrubbing processes, as less steam is consumed, no separate heat-exchange and cooling equipment is required, the quantity of cooling water is greatly reduced, scrubbing agent is not lost, and loss of desired gases by solution is negligible. The process is applicable wherever impure gases are available or are to be used at elevated pressures and temperatures and are saturated with water vapor. It is therefore useful not only for purifying Fischer-Tropsch synthesis gas but also for scrubbing hydrogen and ammonia synthesis gas containing carbon dioxide.

Removal of sulfur from synthesis gas is important to prevent catalyst poisoning. Experiments on the effect of different sulfur compounds are in progress (see fig. 27).

Bench-Scale Experiments

Catalyst-Oil Slurry Process

Like the oil-circulation process described above, the slurry process utilizes oil as an internal coolant. In this case, however, the catalyst particles are small enough so that they are suspended in the oil, if necessary with the help of a suspension aid. The slurry is not circulated outside these laboratory-scale reactors. Because of their lower cost and greater ease of preparation, fused rather than precipitated catalysts were studied during the past year.

Experiments with reduced, fused catalysts showed that induction is necessary for obtaining satisfactory activity of the catalyst. This means that the catalyst is operated initially under rather mild conditions of temperature, pressure, and gas flow and is taken up to normal operating conditions over a period of days. X-ray-diffraction analysis has shown that induction effects virtually complete carbiding of the iron. Replacement of inducted with fresh catalyst during synthesis under normal conditions indicated that the newly added catalyst was inactive and behaved like an inert diluent. When the concentration of active catalyst was varied between about 20 and 100 grams per liter of slurry, very little change in conversion and selectivity of the catalyst was noted above a concentration of 40 gm./l.; between 15 and 20 percent of gaseous product, 55 to 60 percent of gasoline product, and 20 to 30 percent of heavier hydrocarbons were recovered. However, lowering of the concentration of active catalyst below 40 gm./l. resulted in a lower conversion. The conversion could then be increased again by raising the temperature and concomitantly shifting the product distribution until, at a concentration of 20 gm./l., the temperature reached almost 300° C., about 40 percent of the hydrocarbons were gaseous, and no wax was being made.

As was the case with reduced fused, catalyst, induction was found to be desirable for nitrided fused catalyst. For example, a nitrided catalyst that was used under normal synthesis conditions from the very start required a 30° C. higher operating temperature to attain the same activity as an identical but inducted iron nitride. The product distribution or catalyst selectivity, being strongly dependent on temperature, was shifted accordingly. In contrast to the metallic iron in a reduced catalyst, an interstitial phase - iron nitride - is already present in the nitrided catalyst before induction. It is known, however, that sizable amounts of nitrogen are replaced by interstitial carbon during induction.

Iron nitride has been shown earlier to have radically different properties from other iron catalysts, the most remarkable of these being its capacity for synthesizing large amounts of alcohols. Because the slurry process affords ease of temperature control and flexibility of operation, it was used for investigating the possibility of modifying the Fischer-Tropsch synthesis for the production of alcohols. Reduction and nitriding were carried out either in separate equipment or in the reactor under oil. The experiments lasted 1 to 5 months and were either terminated while the catalysts were still active or after the catalysts had been operated purposely under extreme conditions and had thereby lost activity. Light hydrocarbons were recovered in a charcoal absorber (see fig. 28). The variables studied were temperature, rate of gas throughput, and composition and recycle ratio of synthesis gas; maximum possible pressure (300 p.s.i.g.) was always used for obtaining high space-time yields.

When the temperature was varied from 220° to 260° C. in 10° steps, the optimum temperature for production of higher alcohol was found to be 240° C. This maximum yield of 6-carbon alcohol (hexanol) was the result of two opposing trends, increase of low-molecular-weight (water-soluble) and decrease of high-molecular-weight (oil-soluble) products with higher temperature.

Increasing the hourly space velocity of the gas - that is, volumes of gas per volume of slurry per hour - from 200 to 300 resulted in an increased yield of alcohol. Higher space velocities appeared to have little effect.

Reducing the hydrogen-carbon monoxide ratio from 1:1 to 0.7:1 resulted in a lowering of the alcohol yield, while the average molecular weight of the product was increased. Recycling 1 volume of tail gas with 2 volumes of fresh gas gave higher conversion (better utilization) per pass and more alcohol than using fresh gas only.

As much as 60 weight percent of the product consisted of alcohols, most abundant of which was ethanol (about one-third); however, about one-seventh of the alcohol contained hexanol and higher alcohols under favorable conditions. Economic considerations, based upon the current market value of the alcohols, indicate that a small plant, working with natural gas as raw material and utilizing this and the oxo process in succession, would be at least as profitable as a synthetic ammonia plant of comparable size. The alcohols might find use as such (solvents, plasticizers, detergents) or become raw materials for other processes.

In one catalyst-oil slurry experiment, used coolant oil from the Synthetic Fuels Demonstration Plant at Louisiana, Mo., was investigated. This oil contained about 120 grams of finely divided iron per liter as a result of spalling and attrition of the original promoted fused-iron catalyst. The iron was divided about equally between Hagg iron carbide and magnetite. The activity of this slurry was low compared with that of the normal slurries of reduced fused iron, and the temperature of the experiment had to be about 30° C. higher than usual to obtain normal conversion rates. The average molecular weight of the product was lowered correspondingly.

Fixed-Bed-Activity Tests

While the catalyst fines from the Demonstration Plant were tested in the slurry process, the used catalyst particles of normal size were tested in a fixed-bed reactor in which gas is passed through a catalyst bed of such small dimensions that no internal cooling is necessary. Similar bench-scale apparatus is shown in figure 29. After the protective oil was removed with heptane and the catalyst was dried in a stream of carbon dioxide, a 3-week test was made in which the catalyst exhibited normal activity, although production of gas was somewhat higher than usual.

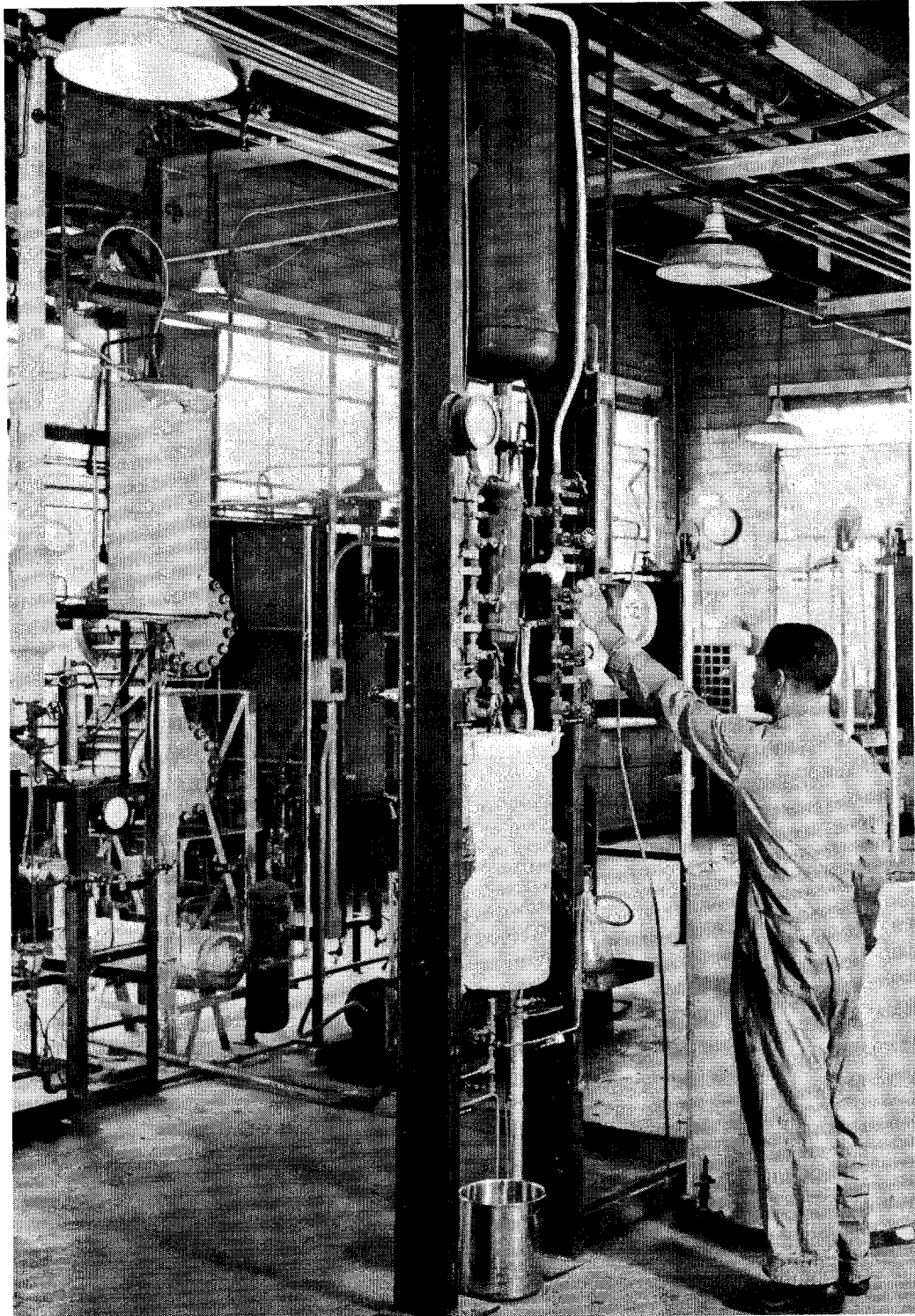


Figure 28. - High-pressure charcoal absorber for recovering light hydrocarbons from spent synthesis gas.

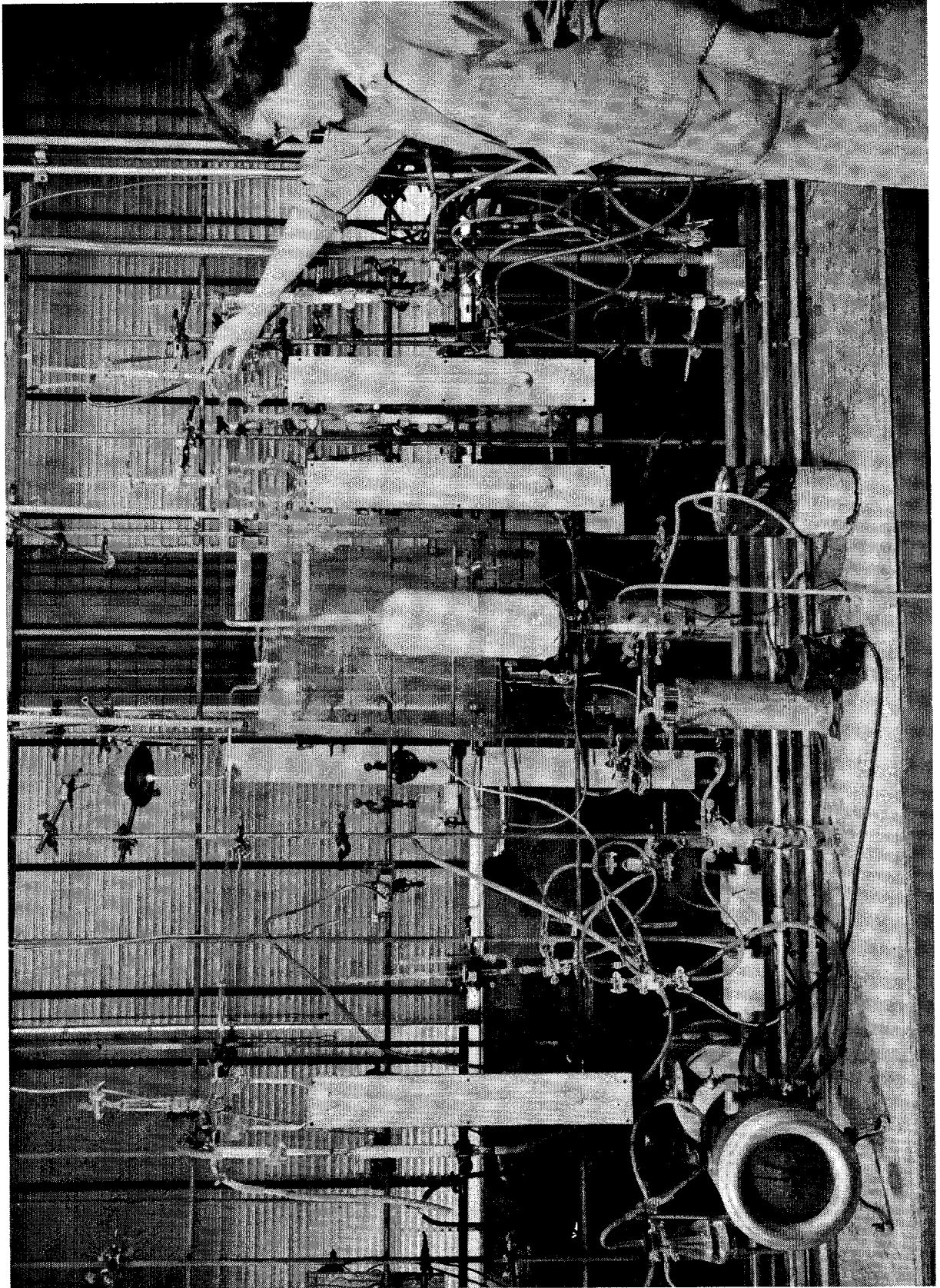


Figure 29. - Bench-scale catalyst-testing apparatus.

A series of tests was made with 6- to 8-mesh fused-iron catalyst, which was reduced to varying extents before synthesis. The object of these operations was to determine the effect of completeness of reduction upon the activity and selectivity of such a catalyst. Up to about 12 percent reduction, both of these properties of the catalyst depended strongly upon the degree of reduction. Beyond 12 percent reduction, the selectivity of the catalyst remained essentially constant (minimum formation of gas); beyond 28 percent reduction, the activity became constant (minimum temperature for desired amount of conversion of synthesis gas). Thus, complete reduction of this size of fused-iron oxide is not necessary for attaining maximum activity and optimum selectivity. In one case, a completely reduced catalyst was reoxidized with steam to about 50 percent. Its activity was as if it had been reduced only 5 percent, while its selectivity was optimum. This experiment, as well as earlier tests of catalysts of different particle size, indicate that the outside of the catalyst particles to a depth of 0.1 to 0.2 mm. is largely responsible for catalytic activity.

Catalyst tests usually are made at constant flow and pressure of synthesis gas, and the temperature is varied to maintain constant conversion. Activity, however, does not vary linearly with temperature, and it is difficult to compare the activity of catalysts, especially if the conversions or flows are not constant; hence, the constant of an empirical-rate equation was used to compare activity in terms of volumes of synthesis gas consumed per volume of catalyst per hour at 240° C. This method permits quantitative comparison of the activities of different catalysts. Its application to batches of fused-iron catalysts, which had been treated in various ways before synthesis, showed that the activity of a carbided preparation was one and one-half times as great and that of a nitrided catalyst twice as great as that of a reduced specimen. The selectivity also varied with pretreatment, of course, the carbided sample producing the least gas and the largest amount of high-boiling product and the nitrided batch producing the largest amount of gas and, as usual, the most oxygenated material.

Mechanism of the Synthesis

Composition of Catalyst and of Synthesis Gas

Role of Promoters

To obtain highly active fused-iron catalysts, small amounts of other chemicals must be added to the iron. These materials (called promoters) may have structural or chemical effects. During reduction structural promoters facilitate the formation of a structure with a large surface area; they stabilize this structure during subsequent treatments and use of the catalyst but, other than effects resulting from the higher surface area, need not influence the catalytic properties. Although chemical promoters do not increase the surface area, they produce large changes in activity and selectivity. Structural promoters - difficultly reducible oxides other than alkali oxides - must be added before fusion of the iron, while chemical promoters - alkali oxides - may be added before or after fusion.

In a series of tests to determine the effectiveness of structural promoters, oxides of the type MO_2 (M being silicon, titanium, manganese, zirconium, or cerium), MO (magnesium, calcium, or copper), or M_2O_3 (boron, aluminum, chromium, or bismuth) were incorporated in batches of the same catalyst. Each sample was divided into two parts; one was reduced and the other reduced and nitrided before synthesis. The 6-week tests were made under identical conditions, except that the temperature was adjusted in all cases to obtain a gas contraction of 63 to 65 percent. Analyses of the products indicated that the effect of these promoters on selectivity was quite

slight. Whereas only titanium and zirconium oxide enhanced the activity of the nitrided catalyst compared with an "unpromoted" sample,^{2/} all but titanium and boron oxide promoted the reduced catalyst. With some exceptions (possibly connected with a change of the state of oxidation during preparation and use), the effectiveness of the promoters decreased in the order MO_2 , MO , M_2O_3 .

Preliminary tests with different alkali oxides (chemical promoters) showed that the activity of nitrided and of reduced fused iron increased with the atomic number of the alkali, that is, in the order lithium, sodium, potassium, rubidium; however, among the nitrided catalysts lithium provided a notable exception, being about as active as potassium. Further work on this problem is in progress.

Behavior of Carbides

Of the known carbides of iron, Hägg iron carbide is commonly found in used catalysts; cementite and hexagonal iron carbide occur only rarely. (A fourth carbide formed during synthesis in a fluidized bed has never been observed at the Bureau.) Cementite is difficult to form under synthesis conditions and, unless preformed, usually appears only if excessively high temperatures prevailed during a test. Hexagonal carbide, on the other hand, tends to change to Hägg carbide during synthesis, except at very low temperatures; it had never been observed in preparations that had been exposed to temperatures higher than about $250^{\circ}C$. However, x-ray and magnetic studies had proved the transformation process to be time- as well as temperature-dependent. Hence it was thought that hexagonal iron carbide may be formed at higher temperatures and, if cooled rapidly enough, may be retained as such. This hypothesis was verified by short-time carburization experiments at up to $350^{\circ}C$. Hexagonal carbide was shown to be present at least up to $325^{\circ}C$. by a method of magnetic analysis developed for this purpose. On the basis of this and previous information, it appears likely that most, if not all, of the carbide made by carburizing iron powder is formed by way of hexagonal carbide; that cementite is formed by way of hexagonal and Hägg carbide; and that deposition of carbide during carburization of iron is the end product of this carbide chain.

The effects of pressure and temperature upon the rate of oxidation of Hägg carbide during synthesis were discussed in the 1951 Annual Report. This work has now been extended to a study of the effect of the flow of synthesis gas. By keeping the hourly space velocity (volume of gas per volume of catalyst per hour) high enough, only 20 percent of the gas was converted. This mode of operations resulted in constant increase of catalytic activity during the first 80 days of synthesis. After the activity had been tripled, it fell quite rapidly and reached its original value after about 100 days of synthesis. The initial rate of oxidation was only one-fourth that of a normally operated catalyst of the same type; this rate decreased to about one-eighth as the test proceeded. Undesirable gas formation was quite low during the experiment. Most of the oxygen (from carbon monoxide) was converted to water rather than carbon dioxide, a verification of earlier observations that water is a primary product of the synthesis and is converted to carbon dioxide by the water-gas shift. The partial pressure of water vapor in contact with the catalyst was calculated to be only about half as much as is usual. This difference may explain the low rate of oxidation of the Hägg carbide.

^{2/} All catalysts were prepared from a highly purified magnetite ore containing a total of 0.5 percent impurities, chiefly silica and alumina. The "unpromoted" preparations were made from this raw material without addition of structural promoters.