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

Research at the Bruceton, Pa., laboratories and pilot plants on the synthesis of liquid fuel from gasified coal (Fischer-Tropsch and related processes), on the production of liquid fuel by hydrogenation of coal (Bergius and related processes), and on the gasification of coal in a vortex reactor has led to developments of theoretical as well as practical importance.

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

Process Development

Pilot-Plant Operations

In the oil-circulation process that has been studied in the pilot-plant stage at the Coal-to-Oil Laboratories of the Bureau of Mines, a mixture of carbon monoxide and hydrogen (synthesis gas) flows upward through the converter, concurrently with the circulating oil, and the synthesis takes place in the expanded (by the flowing oil) bed of catalyst. The heat of the exothermic reaction is transferred to the cooling oil, so that no internal cooling surfaces are needed. Up to now, this process has been carried out in small pilot plants. This year, a barrel-per-day unit has been put into operation (see fig. 28). No unusual difficulties were experienced in running this plant, which is about 13 times larger than those previously used.

To fill the converter to a height of 8 feet, 307 pounds of synthetic-ammonia-type fused catalyst were reduced with hydrogen in two batches. After 98-percent reduction, the catalyst was stored under a low-boiling fraction of synthetic Diesel oil for about one-half year. Induction, which normally requires about 4 days, took 6 days because of trouble with the carbon dioxide-absorption system. When synthesis was started at 254° C., 70 percent conversion was attained at about 450 p.s.i.g., an hourly space velocity of 600 of fresh $0.7H_2:1CO$ synthesis gas, and a gas recycle ratio of 1:1. A decrease in the activity of the catalyst after about 1 week of synthesis probably was caused by relatively large amounts of carbon dioxide in the recycle gas. Installation of a more efficient scrubber and re-reduction of the catalyst made resumption of the synthesis possible. The experiment was terminated after 677 hours. During the test, the usage ratio had increased to about $0.9H_2:1CO$, the concentration of iron in the recycle oil had risen, and the average molecular weight of the product had increased.

A second experiment in the barrel-per-day plant, with $1H_2:1CO$ gas, lasted 1,245 hours. It was terminated because of disintegration of the catalyst, of which only about 45 percent had remained in the converter. The distribution of the liquid and solid hydrocarbons during steady state conditions was 62.4 percent gasoline, 13.9 percent Diesel oil, 10.6 percent heavy distillate, and 13.1 percent wax. After removal of the oxygenates and adjustment of the Reid vapor pressure, the gasoline had an octane number of 77 (unleaded) or 87 (3 cc. TEL added). The Diesel oil, boiling in the range 204°-285° C., had a pour point of 0° F. and a cetane number of 73, which exceeds the premium-grade specification of the Navy by about 20 numbers.

A smaller pilot plant was used to evaluate a fused catalyst, prepared at the Demonstration Plant at Louisiana, Mo., for use there. This catalyst was similar to the commercial synthetic-ammonia-type catalyst used extensively at the Bruceton Station. Initial tests seemed to indicate that the new preparation was not active enough, but subsequent runs showed that the catalyst had been poisoned by the sulfur compounds (fig. 29) in the petroleum fraction which was used as the cooling oil. Although the original petroleum fraction impaired functioning of the catalyst, the used petroleum fraction was not detrimental to the activity, probably because most of the sulfur had been removed in the first operation. When cooled with the used petroleum fraction or with synthetic oil, the catalyst made at the Demonstration Plant exhibited satisfactory activity and mechanical strength.

Laboratory-Scale Experiments

Catalyst-Oil Slurry Process

This process is similar to the oil-circulation process, in that the catalyst is suspended in oil. Unlike the latter process, however, the slurry operation involves use of a powdered catalyst. The modification of the process chosen as most suitable for bench-scale work employs no circulation of slurry outside of the reactor. A number of variables of this process were investigated during the year.

The activity of siderite was unsatisfactory, as only 20-percent contraction of the synthesis gas could be obtained at 300° C., at 100 to 300 p.s.i.g. pressure, and hourly space velocities ranging from 100 to 300.

Two experiments were made with precipitated-iron catalysts. In one run, the dry catalyst was subjected to a "typhoon" induction (high temperature and high space velocity of synthesis gas) in a fluidized reactor (see fig. 30) before synthesis. Synthesis was interrupted after more than 500 hours by mechanical failure, after it had been established that as much as 88 percent of the synthesis gas could be converted at 266° C., 150 p.s.i.g., and an hourly space velocity of 150. Production of undesirable gaseous hydrocarbons was quite low.

The second experiment was begun by inducting the precipitated catalyst in the slurry phase. Synthesis was begun at 100 p.s.i.g. and 253° C. When the pressure was raised to 150 p.s.i.g., the temperature could be lowered by about 30° C. while the conversion was maintained essentially constant. A subsequent increase of the temperature effected almost 90-percent conversion of the synthesis gas. Most of the increased conversion resulted in the production of hydrocarbon gas. A study of the effect of space velocity on the product distribution during this experiment showed that the formation of hydrocarbon gas is not so much a function of temperature as it is of the amount of conversion: At a given temperature, less gas was produced as the extent of conversion was decreased by increasing the space velocity of the synthesis gas.

The difficulties initially experienced with settling of fused catalysts have been overcome. To keep the catalyst suspended in the slurry, a suspension aid - modified bentonite - was added to the oil, producing a gel of higher viscosity than that of the normal slurry. It was thus possible to make uninterrupted experiments for 2 and 3 months. About 75 percent of the oil product boils in the gasoline range, and less than 5 percent is wax. During the first 2,000 hours of one test, for example, about 476 pounds of liquid and solid hydrocarbons and an estimated 28 pounds of oxygenated compounds were synthesized per pound of iron; of the hydrocarbons, 79 percent were in the gasoline range, 13 percent were Diesel oil, and only 2 percent were waxes.

High-Pressure Fixed-Bed Process

The effect of pressure (in the range of 500 to 1,500 p.s.i.g.) on the synthesis reaction was studied with fused iron catalysts (see figs. 31 and 32) that had been nitrided and treated with synthesis gas at high space velocities and lower pressures to avoid the possible clogging of the outlet of the reactor by ammonium carbonate. In one such experiment, the iron carbonitride was used initially at 500 p.s.i.g. and 206°-208° C. After 45 days, during which the pressure was varied between 500 and 1,500 p.s.i.g., a steady synthesis temperature of 241°-242° C. was attained for about 60 percent conversion of the $1.1H_2:1CO$ gas (usage ratio, 0.72-0.75). Comparison with a test at 300 p.s.i.g. showed that the approach to steady-state conditions was apparently independent of pressure. The pressure dependence of the rate of synthesis was found by varying the hourly space velocity (172 to 411) to maintain otherwise constant conditions. This function is expressed by

$$r = k\,p^{\alpha} ,$$

where r = reaction rate (cc./hr.), k = specific reaction-rate constant, p = absolute pressure (p.s.i.), and α = pressure coefficient. While α has previously been found to be about unity in the pressure range 100-300 p.s.i.g., it was 0.72 between 500 and 1,500 p.s.i.g. The effect of pressure on the distribution of products was rather small. As is usual with fused iron carbonitride catalysts, the percentage of oxygenated products was high but did not change markedly with pressure. There was a slight tendency toward production of less methane and more liquid material at higher pressures. At the same time, the average molecular weight of the liquids and waxes appears to have been lowered somewhat by raising the pressure. Further tests are in progress to study the effect of pressure on synthesis with reduced fused catalysts.

Catalyst-Activity Tests

Of the factors that determine the quality of a gas-synthesis catalyst, origin, and storage and pretreatment effects were studied (fig. 33). A commercially available iron fluoride showed no activity. A low-cost iron ore was active but produced so much methane as to be worthless for the synthesis of liquid fuels. Several catalysts were prepared from mixtures of magnetite, potassium carbonate, and ball clay in different proportions. These catalysts had high mechanical strength but operated at relatively high temperatures and in most instances produced predominantly gaseous hydrocarbons. After nitriding, one of these preparations operated 20° C. lower than previously (for the same contraction) and produced 20 percent more gas.

The effect of storage under oil on the activity and selectivity of a synthetic-ammonia-type catalyst was negligible for storage periods as long as 6 months. No difference was found between the storage qualities of crude synthetic oil (made with an iron catalyst) and of oil washed with caustic to neutralize any acid, washed with water to remove the caustic, and dried to produce a dry, neutral oil.

Cementite was prepared by four different methods, using a fused catalyst, and the effect of the method of preparation on the synthesis was investigated. Partial carburization of the iron to Hägg carbide and subsequent homogenization (cementite formation) by annealing produced the most active of these catalysts for use at 100 p.s.i.g. pressure. Direct formation of cementite by carburization with methane and annealing to cementite of a mixture of Hägg carbide and metallic iron in a used catalyst yielded catalysts of lower activity. However, the presence of magnetite in the used catalyst may have had an unfavorable effect. At 300 p.s.i.g. there was no appreciable difference in activity between cementite prepared by homogenization of a mixture of Hägg carbide and metallic iron and cementite made by "typhoon" induction (see Catalyst-Oil Slurry Process).

The activities of reduced, normally inducted, and "typhoon" inducted, precipitated catalysts were also compared. "Typhoon" induction produced a remarkably active catalyst. This enhanced activity may be due in part to increased surface resulting from mechanical disintegration of the catalyst during its induction. The production of gaseous hydrocarbons was very low.

Reaction Mechanism Studies

Catalyst Composition and Reactivity

Further studies were made of the chemical properties of iron carbides, which, while not necessarily catalysts themselves, are always formed as byproducts of the synthesis and appear to have a profound effect on the activity of iron catalysts. The rate of carburization with carbon monoxide of two widely different types of catalyst obeyed the equation

$$-d(\mathrm{Fe})/dt = k(\mathrm{Fe})^2$$

at least up to about 50 percent carbiding and at gas velocities where transport cannot be a limiting factor; here t = time, k = specific reaction-rate constant, and (Fe) = mole fraction of metallic iron remaining. This rate law permitted determination of the temperature and pressure dependence of the initial rate of carburization. The activation energies varied between 27 and 32 kg.-cal. per mole, and the exponential factors for the pressure dependence varied between 0.2 and 0.3, depending on the catalyst.

The effect of alkali on carburization of reduced iron catalysts over a range of alkali concentrations and carburization temperatures was to decrease the rate of carbide formation (at least after about 50 percent of the iron had been carburized), to increase the rate of carbon deposition (after carburization was essentially completed), and to decrease the rate of reduction

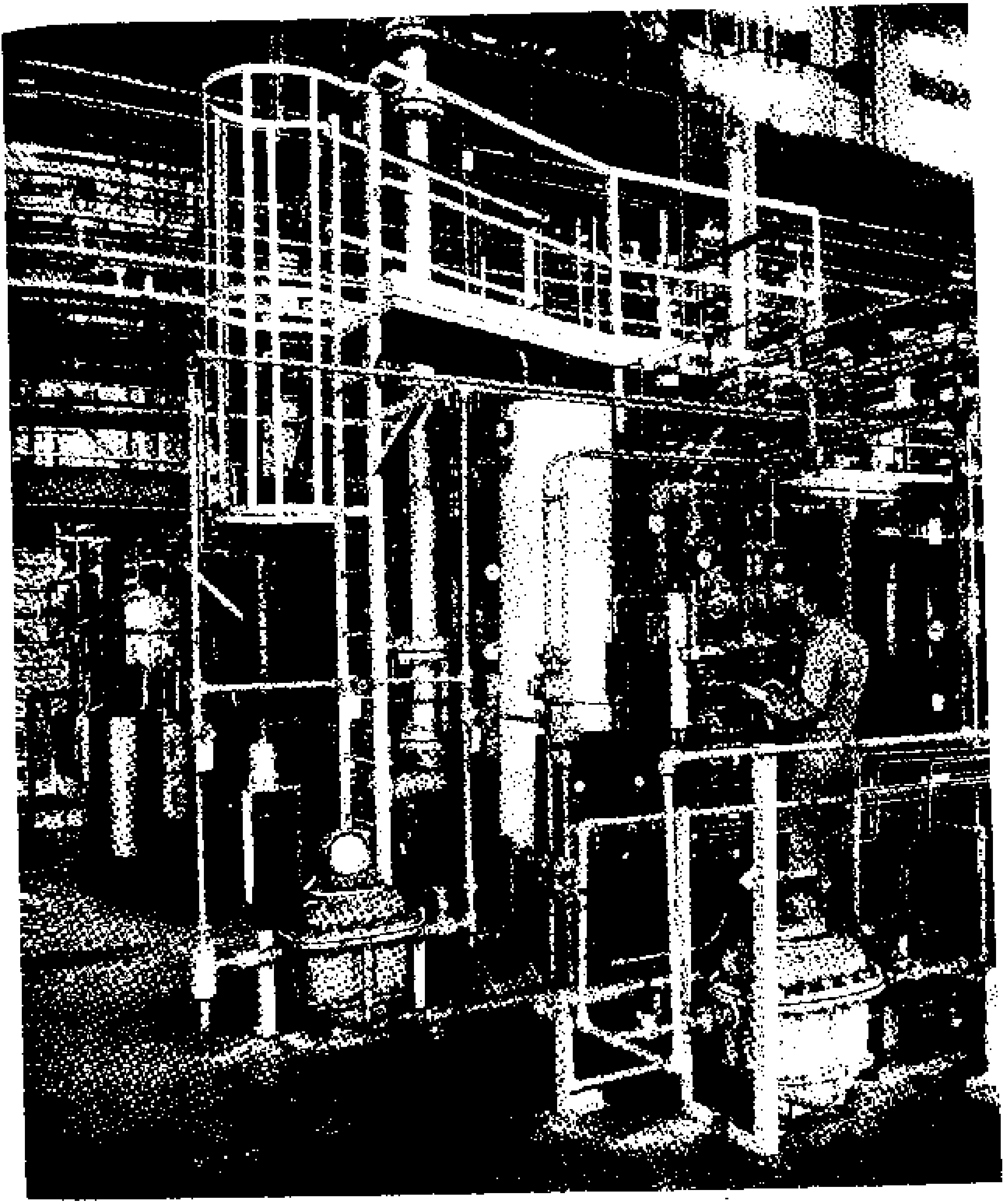


Figure 28. - Barrel-per-day Fischer-Tropsch plant.

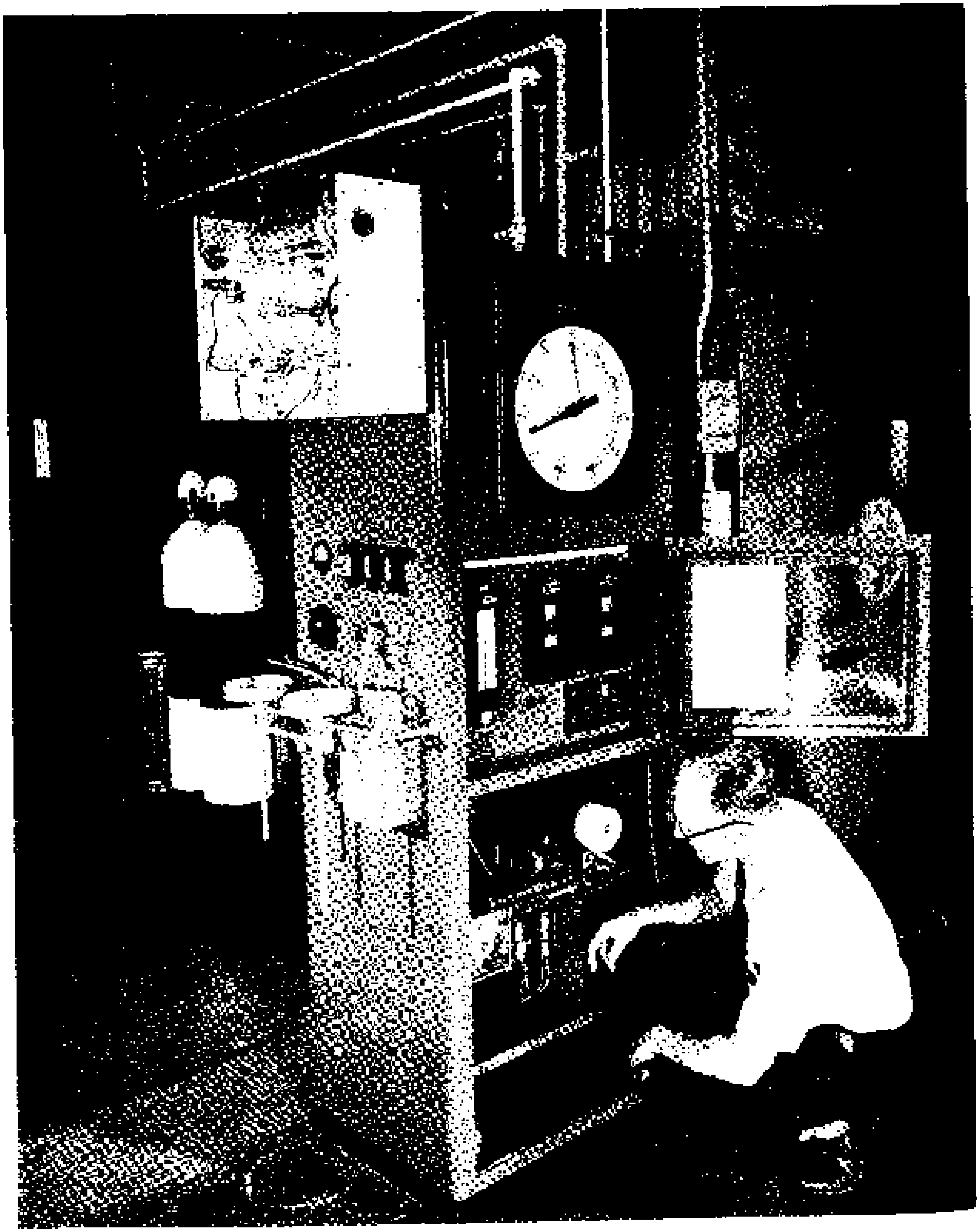


Figure 29. - Hydrogen sulfide analyzer.

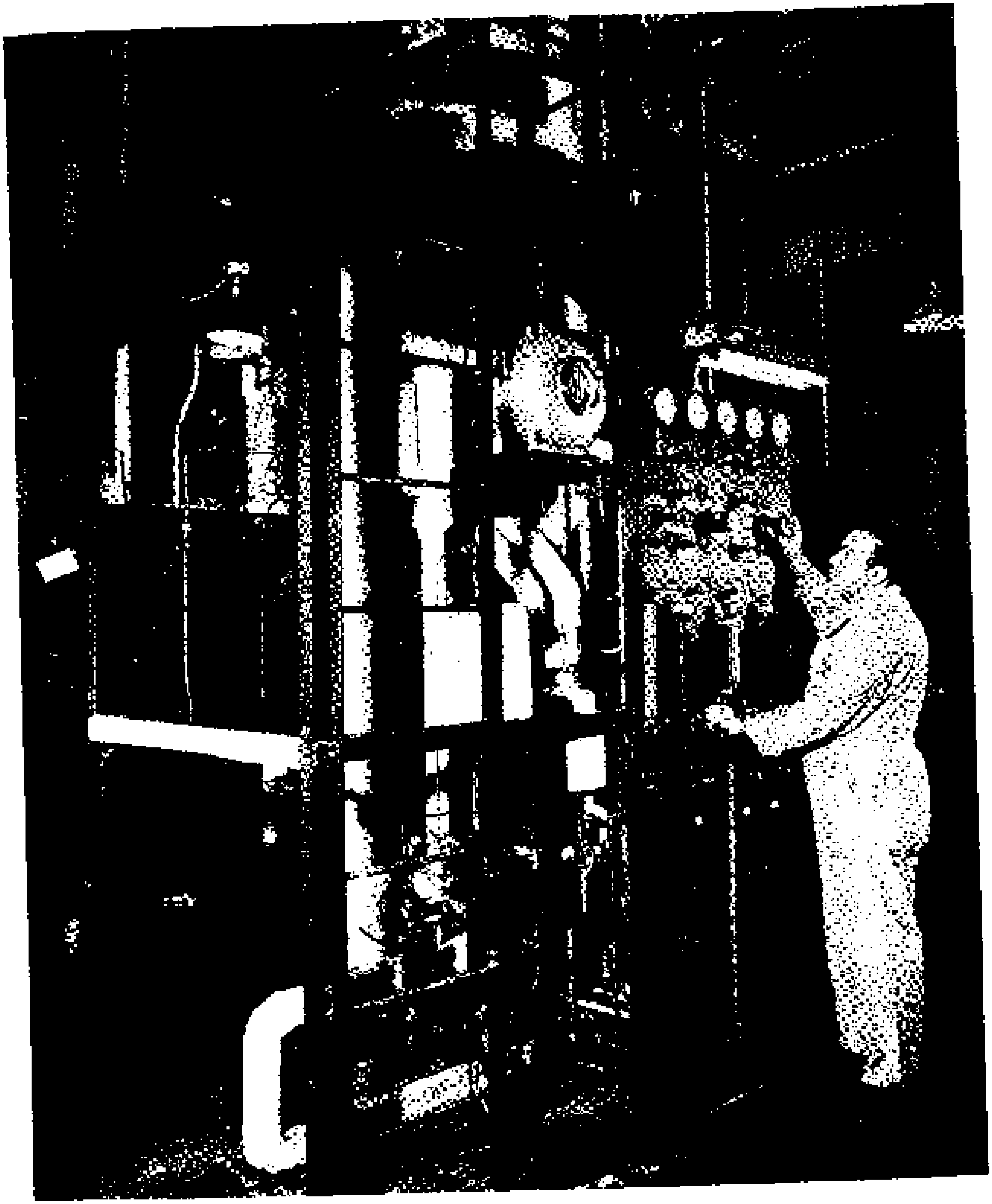


Figure 30. - Unit for fluidized Fischer-Tropsch process.

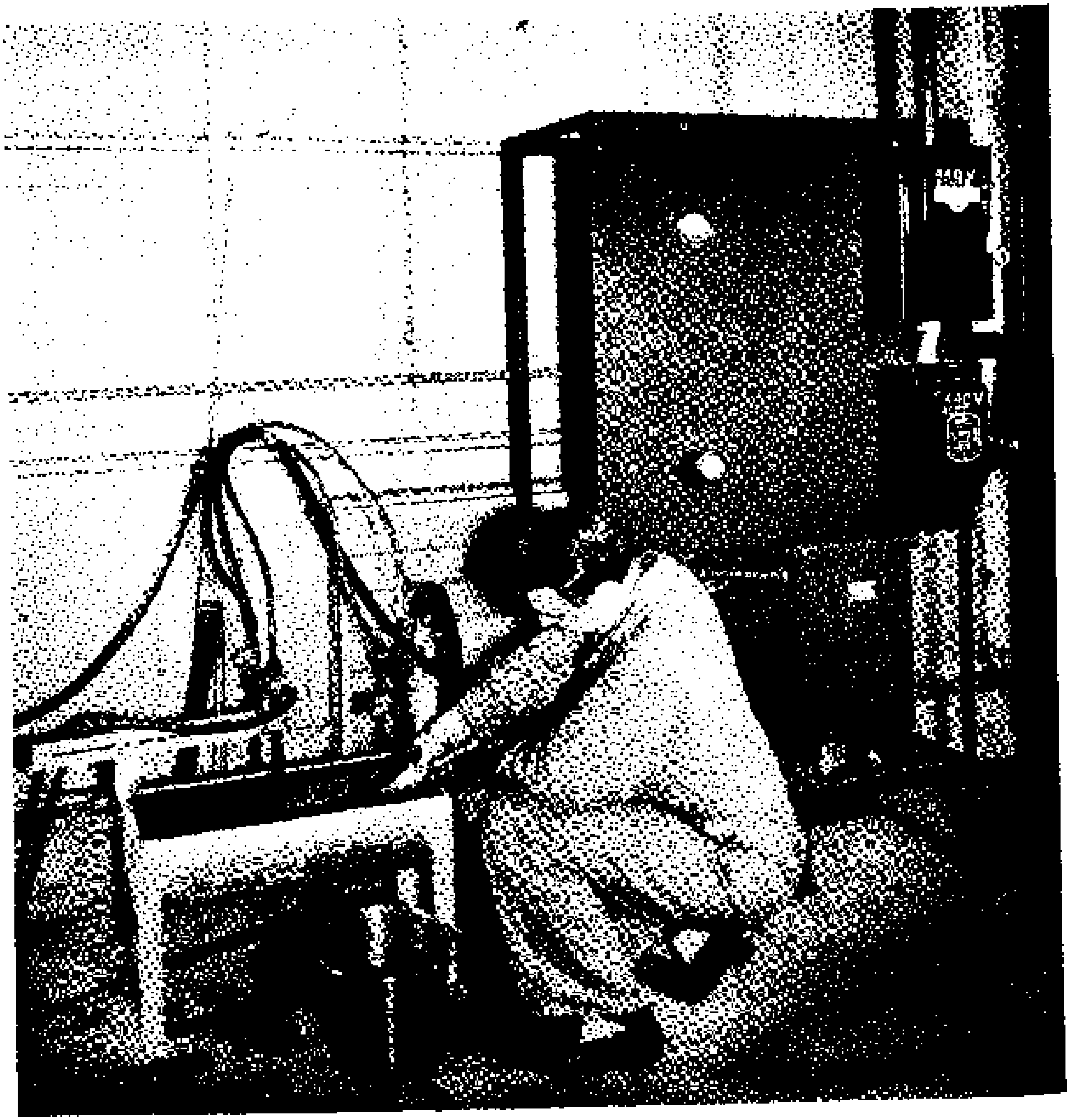
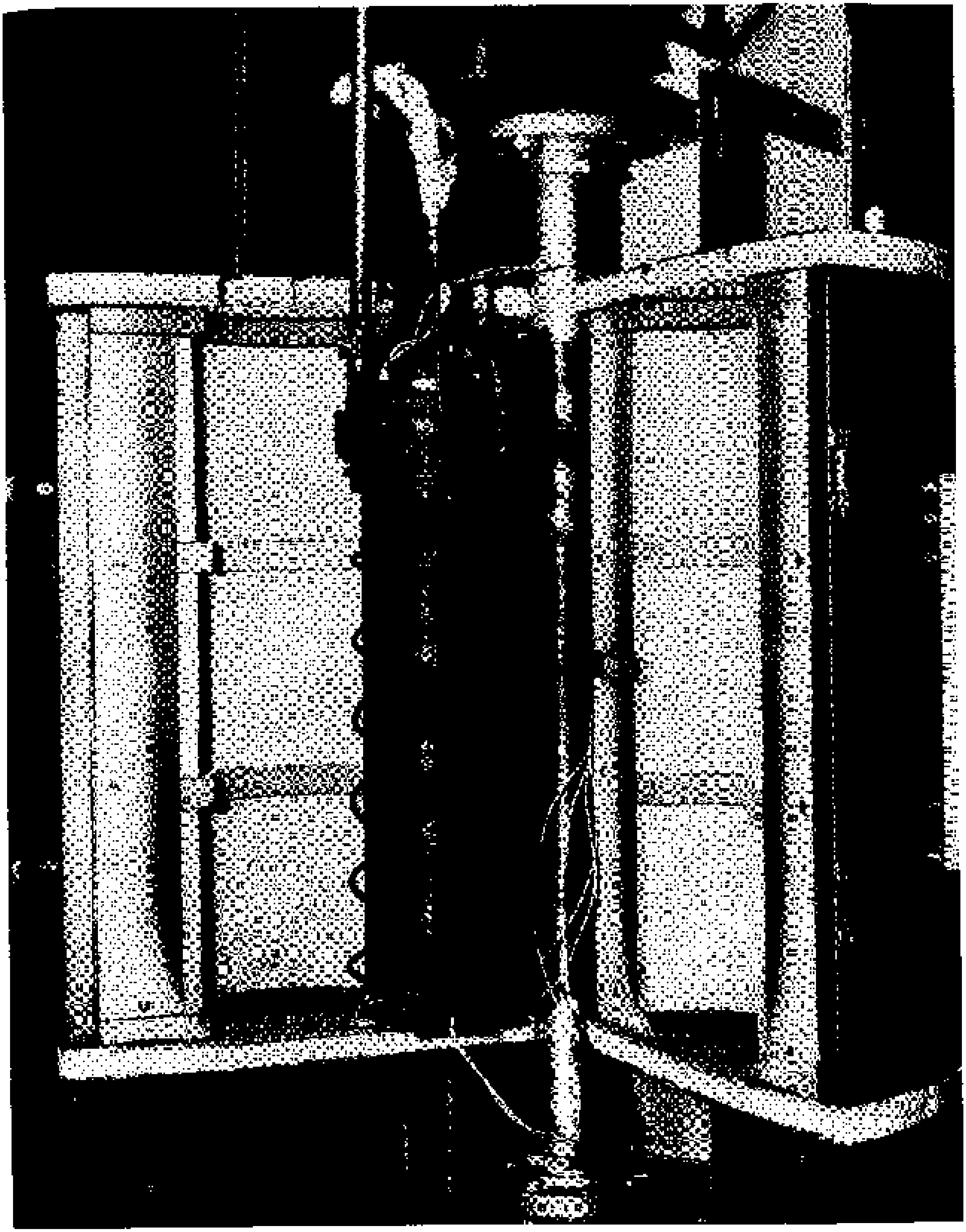


Figure 31. - Small fusion unit.



212686 O - 52 - 8

Figure 32. - Steel-shot oxidation unit.

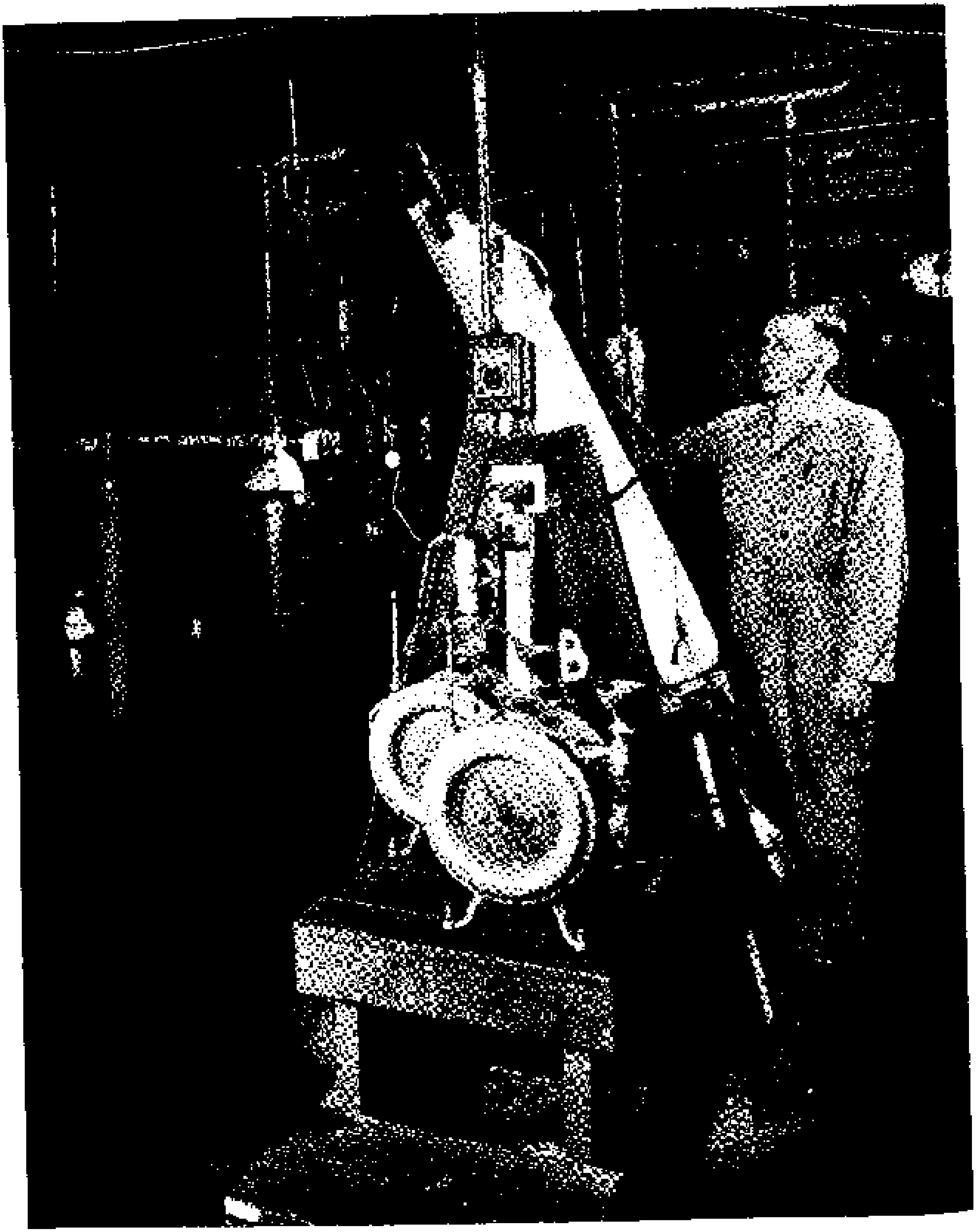


Figure 33. - Tilting reduction furnace.