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.

High-pressure fixed-bed experiments. - 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.

Thermal cracking of high-molecular-weight products. - 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.

Although in most of the work done on the OXO process olefins were used as raw material, it has been demonstrated that olefins are not necessary intermediates in this reaction. Thus, methanol reacts rapidly to yield chiefly ethyl alcohol, wher benzyl alcohol reacts to yield about 25 percent of β-phenylethyl alcohol. For these two reactions, an olefin intermediate obviously could not have been formed.

In the presence of a cobalt catalyst, the order of reactivity of various star ing alcohols under OXO conditions was determined to be tertiary > secondary > prim The simplest primary alcohol, methyl alcohol, however, was found to be anomalous, i that it reacts with synthesis gas more rapidly than secondary alcohols. The absenc of appreciable quantities of higher alcohols in the products from the reaction of methanol indicate that ethanol probably would react sluggishly in the homologation reaction. This was confirmed by experiment; a 4.1 percent yield of n-propanol and small quantities of butyl alcohols were obtained after a long period of reaction. It is interesting to note that the variety and distribution of products obtained from methyl alcohol in the homologation reaction have certain similarities to the oxygenated products obtained in the Fischer-Tropsch process. Ethanol is the chief oxygenated product from the Fischer-Tropsch reaction, and relatively small quantities of methyl, propyl, and butyl alcohols are found. The preponderance of ethanol and relatively small amounts of methanol, n-propanol, and butanols in the Fischer-Tropsch products may be significant in comparison with the rapid conversion of methanol and the slow reaction of ethanol, which are characteristic of the homologation reaction.

An important feature of the OXO reaction is the isomerization of the olefin being subjected to the reaction. There is apparently a competition between hydroformylation (the addition of H and CHO across the double bond) and isomerization of the double bond. This isomerization probably is a free-radical reaction catalyzed by dicobalt octacarbonyl. In substantiation of this mechanism, experiments showed that isomerization took place when cobalt carbonate was used as catalyst, but that when cobalt acetate was used, no isomerization occurred. The difference between the behaviour of these two catalysts is thought to stem from the inability of the acetat to form the free radical initiator, dicobalt octacarbonyl, unless hydrogen is presen Cobalt carbonate, however, can form the carbonyl without hydrogen. These facts may be of practical importance, in that a compound with a terminal double bond may be converted into one with an internal double bond and the resulting compound treated with synthesis gas to give only branched compounds. Both the homologation of alcohols and the isomerization of olefins are unaffected by sulfur compounds. This is consistent with the postulated free radical mechanism of these reactions.

Under the conditions of the OXO synthesis, α-, β- unsaturated aldehydes are not hydroformylated but are reduced to the saturated aldehydes at 125° C. and then to the corresponding alcohol at higher temperature. Aromatic aldehydes, ketones, and alcohols yield at 180° C. under OXO conditions, chiefly hydrocarbons. The hydrogenation of aromatic ketones and aldehydes occurs, probably by a stepwise mechanism with the aromatic carbonyl compound reduced first to the alcohol, followed by reduction of the alcohol to the hydrocarbon. The ready reduction of aromatic alcohols to hydrocarbons and the occasional isolation of the intermediate alcohol support this view. Previous work has shown that aliphatic aldehydes and ketones are reduced to the alcohol stage under the same conditions. If the reduction is a homogeneous reaction that proceeds via a free-radical mechanism, hydrogenation under these conditions should not be adversely affected by sulfur compounds, as is the heterogeneous catalysis of hydrogenation over a solid catalyst. Indeed, it was found that 2-thiophenealdehyde treated with synthesis gas at 180° to 185° C. was readily reduced in good yield to a mixture of 2-thenyl alcohol and 2-methylthiophene.

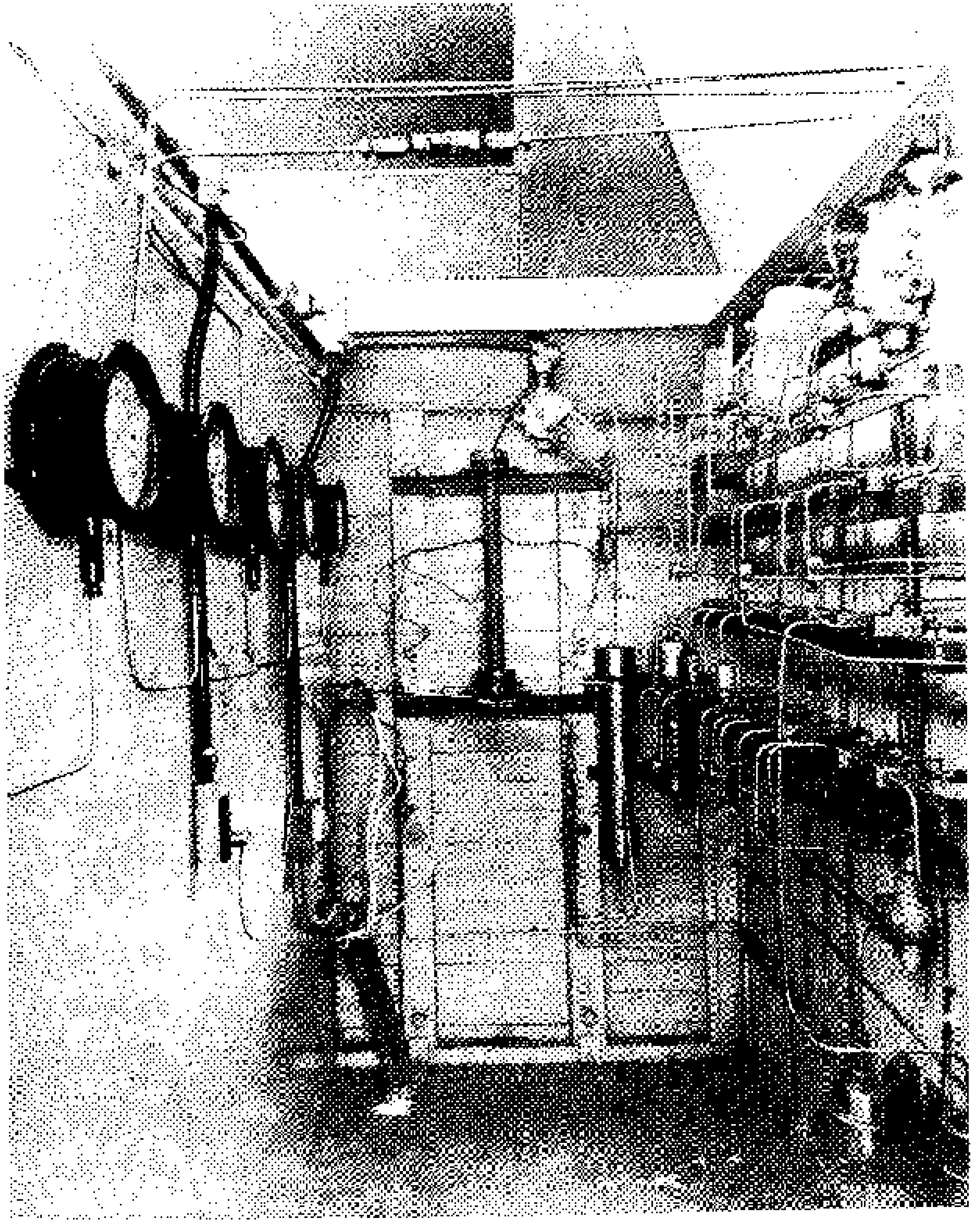

Figure 37. - Continuous OXO unit.

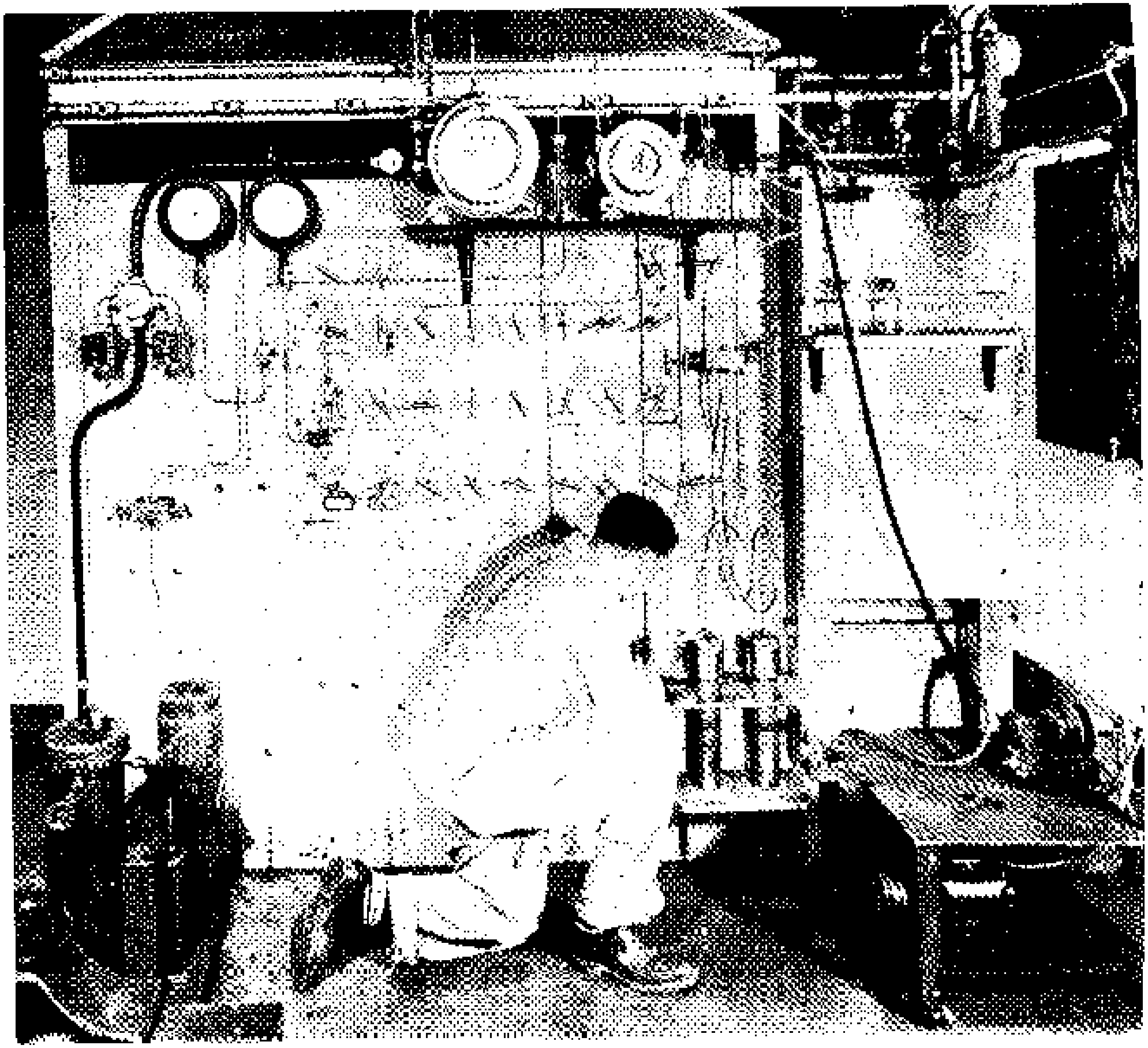

Figure 38. - Control panel for continuous OXO unit.

Attempts to reduce nitro compounds with synthesis gas under OXO conditions produced the following results: When nitrobenzene was treated with synthesis gas at 185° C. in the presence of cobaltous acetate, no reaction occurred, nor did reaction occur when cobalt carbonate was used. Examination of the reaction products in both instances revealed that the cobalt salt had not reacted to form cobalt carbonyl, the essential catalyst for the reduction. Addition of nitrobenzene in small amounts to octene-1 and cobalt acetate was found to prevent the OXO reaction from taking place. Small amounts of nitrobenzene also prevented the reduction of aldehydes and ketones. In both cases, no cobalt carbonyl was formed from the cobalt salt used as catalyst. However, when small amounts of nitrobenzene were added to a solution of preformed dicobalt octacarbonyl in octene-1, the OXO reaction took place at the usual temperatures and at the usual rate. It is evident, therefore, that nitrobenzene prevents the formation of cobalt octacarbonyl from cobalt salts but does not interfere with the usual catalytic action of cobalt carbonyl. Equipment employed in studying the homologation reaction is shown in figures 37 and 38.

Primary Oxygenated Products from Iron Catalysts

In synthesis over iron catalysts most of the oxygen consumed appears as carbon dioxide. It is of interest in determining the mechanism of the synthesis to ascertain whether this carbon dioxide is a primary product of the reaction

$$2nCO + nH_2 = (CH_2)_n + nCO_2$$

or whether water is the primary oxygenated product, forming carbon dioxide by a secondary water-gas shift reaction,

$$\begin{array}{c} nCO + 2nH_2 = (CH_2)_n + nH_2O \\ \underline{nH_2O + nCO = nCO_2 + nH_2} \\ 2nCO + nH_2 = (CH_2)_n + nCO_2 \end{array}$$

Laboratory-scale experiments using synthetic-ammonia-type catalyst showed that the ratio of water to carbon dioxide in the product was distinctly higher when the water was continuously removed by freezing than when the circulating gases were allowed to become saturated with water vapor at room temperature. Under these conditions, the partial pressure of water did not exceed 30 mm., or about 3.5 percent of the total pressure, even at the end of the catalyst bed. The data show that the fraction of total oxygen going to water is about twice as great for the two experiments in which water was continuously removed as for the three experiments in which it was allowed to saturate the system. In the latter experiments, the average feed gas was rich in hydrogen and the product high in carbon dioxide. The small partial pressure of water appears to have been more than enough in these cases to overbalance the effect of enrichment in hydrogen. The results indicate strongly that at least part of the carbon dioxide in the products arises from a secondary water-gas-shift reaction, and, furthermore, that the partial pressure of water need not be very high for this reaction to take place at a considerable rate.

Participation of Olefins in the Synthesis

Laboratory-scale experiments designed to demonstrate to what extent butene-1 (and olefins in general) participates in the synthesis of hydrocarbons from carbon monoxide and hydrogen showed that over both cobalt and iron catalysts the principal reaction of butene-1 was hydrogenation to butane. The butene was relatively more reactive on the cobalt than on the iron, but in no case was a high degree of conversion to pentene observed. Although the quantities involved in these experiments were too small to be regarded as accurate results, from the practical viewpoint it seems likely that the addition of large amounts of low-boiling olefins to normal synthesis gas in an effort to convert the olefins to heavier products will result in a high degree of hydrogenation.

Characterization of Products from the Hydrogenation of Carbon Monoxide

Characterization of the products obtained from the Stanolind Fischer-Tropsch process - which differs from the processes being studied in the Bureau laboratories, in that a fluidized bed of catalyst particles is employed - has been continued along two lines. As the result of consultations with the Standard Oil Co. of Indiana, it was agreed that detailed examination of these products would be confined in the Bureau laboratories to the olefinic and aromatic components, those fractions on which the Bureau and Standard Oil data were not agreed. Accordingly, with the help of product samples and laboratory data supplied by the Standard Oil Co. of Indiana, Bureau research on the olefinic constituents has been completed, and that involving the aromatic constituents is well under way.

The development of a method for the separation of the aromatic portion of the oil products involves adsorption of the oil fraction under investigation on silica gel followed by elution with the proper combination of solvents. Following the separation of the aliphatics from the oxygenated compounds and aromatics by silica-gel adsorption, the total olefin contents of the distilled Stanolind fractions were determined as the average of three methods, namely, hydrogenation, bromine number determination, and infrared analysis. These results, recalculated to the original fractions, were in substantially good agreement.

The results obtained by applying these analytical procedures to the original, untreated fractions disagreed, understandably, because of the presence of oxygenated compounds. Hydrogenation and determination of the bromine number of untreated samples produced results that were prohibitively high; those from the infrared method, which does not suffer as much from the interference of oxygenated compounds, were much lower. In fact, the results obtained by infrared analysis of untreated fractions are generally low compared to the original data on the corresponding treated samples, but they are in fair agreement. The largest discrepancy was found in the fraction boiling from 100° to 150° C.; an olefin content of 61.1 percent was obtained as an average of the three methods on the treated fraction, and an olefin content of 51.5 percent was obtained by infrared analysis of the untreated fraction.

Infrared data also have been obtained for a fractionated product from the internally cooled converter and have been calculated to the same basis as those of the Stanolind product fractions. These data not only give value for total olefins but also provide a breakdown into terminal, internal, and branched terminal olefins. A direct comparison between the infrared data for the product from the internally cooled converter and those for Stanolind product shows that the percentage of total olefins is higher in the Stanolind fractions with terminal and branched-terminal olefins predominating. Internal olefins are present in the Stanolind fractions in very small concentrations and are appreciably less than the internal olefins present in the fractions from the internally cooled converter. A study of the contents of

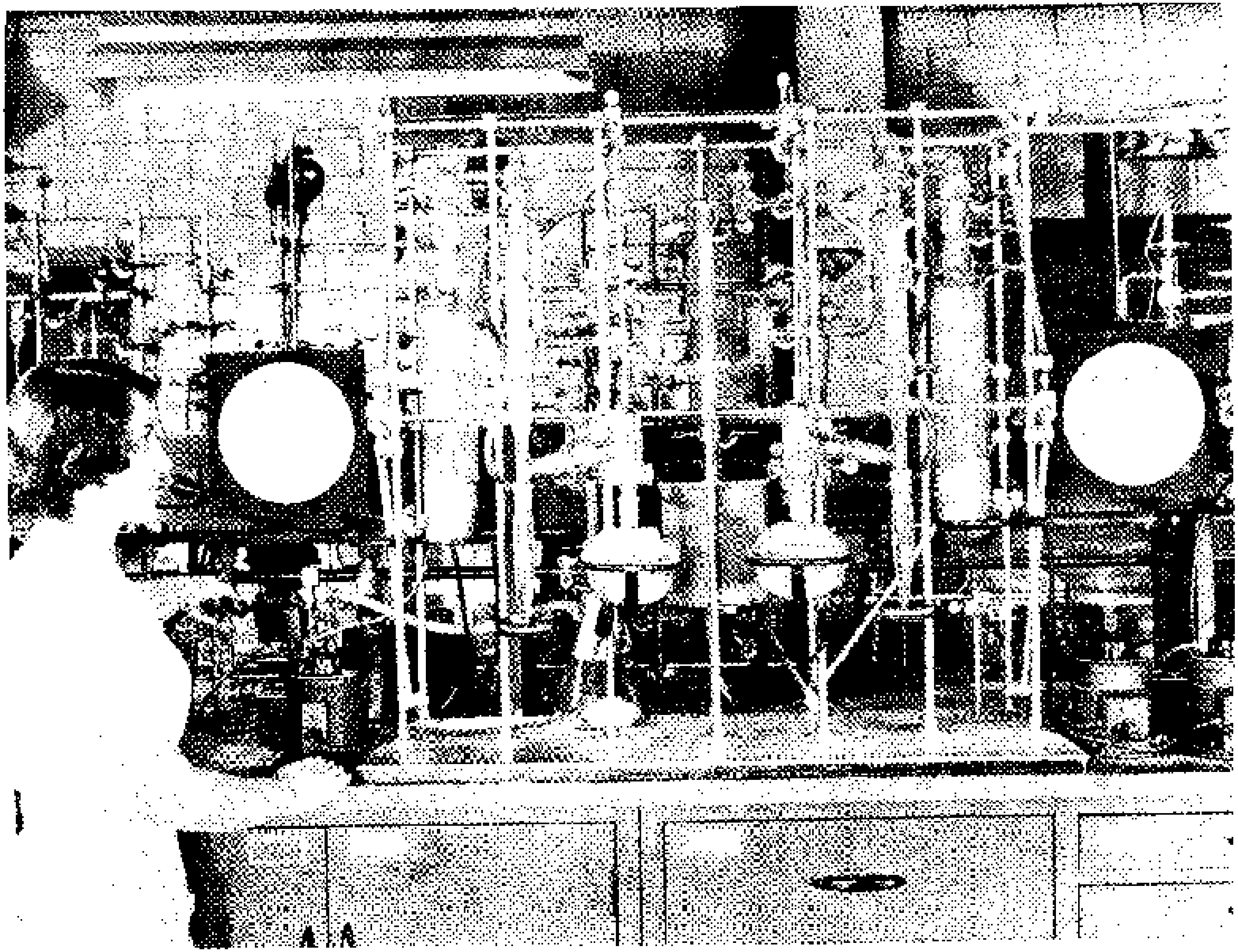

Figure 39. - Vacuum-distillation equipment for characterizing Fischer-Tropsch products.

Figure 40. - Computing room for working up spectrometric data.

ketones and/or acids, esters, and alcohols in the products of the two processes reveals that the Stanolind product is significantly richer in ketones and/or acids and esters, particularly in the higher-boiling fractions. The lower alcohol contents of the Stanolind fractions may be attributed to water-washing of the product and operation at higher temperatures.

Comparison of the weight-percent distribution of the products from the Stanolind and internally cooled converter processes is interesting. The maximum amount of the Stanolind product (26.4 percent) boils in the range 60° to 100° C., whereas the product from the internally cooled converter yields a maximum (12.4 percent) in the range 100° to 150° C. (Although a value of 15.7 percent was obtained between 0° and 60° C. for the product from the internally cooled converter, this includes the C_4 hydrocarbons obtained from the charcoal-trap liquid. The Stanolind product was stabilized to eliminate these compounds.) The amount of residue (that fraction boiling above 320° C.) was found to be much larger for the product from the internally cooled converter (36.2 percent) than for the Stanolind product (6.8 percent). Distillation equipment is shown in figure 39.

Investigation of a method for converting isobutene and isopentenes into the respective chlorides, which are separated from the remaining mixture of hydrocarbons before it is analyzed by means of the mass spectrometer, suggests that this technique may be applied to the analysis of products from the Fischer-Tropsch synthesis. Such an analysis has been complicated heretofore by the similarity of the mass spectra of the butene compounds. The role played by spectrometric techniques in the characterization of Fischer-Tropsch products has been most important (see fig. 40). Much of this analytical equipment has been shown in previous annual reports.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

Pilot-plant Operations

Fuel-oil production. - The liquid-phase coal-hydrogenation pilot plant was operated with a series of catalysts to determine their relative efficiencies for the hydrogenation of Rock Springs coal at 460° C. and 1,500 p.s.i. to produce a heavy fuel oil. Using a coal-oil paste containing 35 percent of coal, the results indicated that these catalysts, when impregnated on the coal, were decreasingly effective with respect to coal liquefaction and asphalt removal, in the following order: Ammonium molybdate, stannous chloride, nickelous chloride, and ferrous sulfate. Comparison of these results with the yields obtained in tests made at 3,500 p.s.i. show that the liquefaction of coal is increased significantly with pressure. This procedure for production of a No. 5 or 6 fuel oil at 1,500 p.s.i. is quite operable and may be important in emergencies for fuel-oil production in places like Australia or South Africa, where coal but no petroleum deposits exist.

Middle-oil production. - The liquid-phase pilot plant was then operated to produce a middle-oil product using the most efficient catalyst of the series, ammonium molybdate, and maintaining the heavy-oil trap at a temperature of 300° C. Using a molybdenum concentration of 0.5 percent impregnated on Rock Springs coal and maintaining conditions of 460° C. and 1,500 p.s.i., a "middle-oil" product was obtained that ranged from 30 to 36 percent, based on moisture- and ash-free (m.a.f.) coal. In addition, about 13 percent more centrifugal heavy oil was obtained (27 percent more based on m.a.f. coal) than was required for preparing the paste pumped into the high-pressure plant. About half this excess heavy oil was collected as excess