Chemical analysis (table 22) showed that the chloride content of the inactive ferric-iron catalysts was at least 20 times greater than that of the active ferrous-ferric preparations. On the basis of this information and additional data obtained by X-ray diffraction analysis, the following explanation of the deactivating effect of chloride is proposed.

TABLE 22. - Effect of presence of chloride in precipitated iron catalysts upon their activity in the Fischer-Tropsch synthesis
(SHV = 100, pressure = 7 atmospheres)

| Catalyst No. | Composition | Synthesis temperature, °C. | Contraction, percent | Average $C_{5+}$ hydrocarbon yield, g./m3a/ | Chloride, percent of raw catalyst |
|---|---|---|---|---|---|
| L3004 | $75^{+2}$-25$Fe^{+3}$-20Cu-0.2$K_2CO_3$ | 229 | 66 | 88.3 | 0.04 |
| L3008 b/ | 100$Fe^{+2}$-20Cu-.5$K_2CO_3$ | 239 | 53 | 75.8 | .02 |
| L2001 | 100($Fe^{+2}$+$Fe^{+3}$)-0.2$K_2CO_3$ | 238 | 64 | 73.8 | c/ |
| L2003 | 100$Fe^{+3}$-0.2$K_2CO_3$ | 263 | 28 | 16.0 | .56 |
| L3006 | 100$Fe^{+3}$-10Cu-0.2$K_2CO_3$ | 282 | 37 | 12.7 | .92 |

a/ G./$m^3$ of feed gas.
b/ Catalyst disintegrated.
c/ Precipitated from nitrates.

1. In the presence of chloride and ferric iron alone, $\beta$ $Fe_2O_3.H_2O$ was produced, which retained chloride in the crystal structure. During synthesis, chloride present on active centers deactivated the catalyst.

2. In the presence of chloride and ferrous and ferric iron (at least 35 percent $Fe^{+2}$) or ferrous iron alone, the formation of $\beta$ $Fe_2O_3.H_2O$ was inhibited. Instead, magnetite, $Fe_3O_4$, or ferrous hydroxide, $Fe(OH)_2$, or a mixture of both, was formed; from this crystal structure, chloride was easily removed by washing.

## Catalyst Activity and Durability

The mechanical stability of new catalysts and the control of wax concentration in the recirculated oil are being investigated in the laboratory in connection with the internally cooled, oil-circulation process. Progress is being made towards an early solution of the problem of very cheap, durable, and adequately active catalysts for the internally cooled process. Because of the relatively expensive and difficultly reproducible nature of the fused, synthetic-ammonia type of iron catalyst, the use of readily available iron ores and industrial byproduct iron oxides is being studied. Starting with either finely divided magnetite ore concentrated by magnetic separation, or with mill scale from the steel industry, active and durable catalysts were prepared. The preparation consisted in making a thick paste of the finely powdered iron oxide with an aqueous solution of the nitrates of promoters such as aluminum, potassium, magnesium, and calcium, extruding the paste into small rods about 3/16 inch by 1/2 inch, drying, sintering (local fusing) at 500° to 600° C., crushing to 8- to 10-mesh, and reducing with hydrogen. Catalysts so prepared were found to be much more active than the fused synthetic-ammonia type. They were not, however, sufficiently resistant to mechanical disintegration by the hydraulic action of the circulating oil in the internally cooled reactor. Improved mechanical stability is being sought by the addition of binders such as clay, silica gel, etc. The cost of these catalysts will not exceed about 5 cents per pound. Alkali-impregnated glomerules made from iron-oxide powder also appear to merit further investigation. The wet iron-oxide powder is compacted with a high-frequency vibrator, rolled into rough spheres, sintered at 1,200° C., and impregnated with alkali. After reduction at 450° C. for 20 hours, the glomerules were operated in the synthesis at a temperature of 235° C. In general, the production of $C_{4+}$ hydrocarbons increases with the alkali content of the catalyst up to about 2.1 parts of $K_2O$ per 100 parts of Fe. A fused iron catalyst containing 2.76 $K_2O$ per 100 Fe was found to be relatively inactive (operating temperature about 300° C.). With cemented catalysts, the optimum concentration of $K_2O$ appears to lie between 0.5 and 1.0 parts per 100 Fe.

Magnetite powder cemented with 5 percent of borax, heated to 800° C. for 10 minutes, followed by reduction at 450° C. for 20 hours, was operated in the synthesis at 250° C. This type of catalyst has hitherto been described as "sintered" instead of "cemented", but in the patent literature the term "sintered" is usually applied to catalysts in which the active component has been modified drastically by heat. In the present catalyst, the particles of iron oxide are cemented into granules by the borax, and no such drastic change is considered as taking place.

Work has continued on the duplication of the German synol catalyst ($Fe-Al_2O_3-CaO-K_2O-SiO_2$), which was found to be much more active than the usual synthetic-ammonia type catalysts, comparing favorably in activity and product distribution with the best precipitated catalysts. Previous attempts to duplicate the synol catalyst have been unsuccessful. Recently, however, information was found in captured German documents indicating that the best German synol catalyst was made by re-fusing an ammonia-type catalyst with carbonyl iron. The only significant differences between the preparation and composition of the synol catalyst and those of the usual synthetic-ammonia type catalysts are that (a) the synol catalyst contains calcium oxide in addition to the usual promoters; (b) the synol catalyst was remelted, and carbonyl iron was added to the melt; and (c) the synol catalyst was in the form of a fine powder. Comparison of the synol catalyst with synthetic-ammonia type catalysts of various particle sizes and containing as much as 30 percent carbonyl iron has demonstrated that (b) and (c) can explain most of the greater activity of the synol catalyst. Thus, the activity of a fused catalyst appears to vary inversely with the particle diameter, and it appears that accessibility of the catalyst surface is an important factor in the Fischer-Tropsch synthesis. This conclusion is supported by the results of mercury- and helium-density measurements.

## Study of Fundamental Properties of Fixed and Fluidized Beds

### Heat Transfer Through Fluidized Beds

A study of the physics of heat transfer through fluidized beds of round and sharp silica sands and iron Fischer-Tropsch catalysts was completed.[89]

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[89] Leva, M., Grummer, M., Weintraub, M., and Storch, H. H., A Study of Fluidization of an Iron Fischer-Tropsch Catalyst: Chem. Eng. Progress, vol. 44, 1948, pp. 707-716.

## Flow Through Fixed Granular Beds

A monograph has been completed for the calculation of pressure drop across fixed particle beds for viscous fluid flow; similarly, a correction chart has been prepared for the transitional range where viscous flow changes to turbulent flow. A general pressure-drop formula has been found to be valid for the laminar, transitional, and turbulent regions of fluid flow through fixed beds of any particle size. This work was done in connection with the accurate estimation of the energy requirements of the Fischer-Tropsch hot-gas-recycle process and other processes in which large linear velocities of gases through packed tubes are necessary.[90] Equations were derived that permit the evaluation of shape factors for ring or cylindrical packings.[91]

## Flow Through Fluidized Beds

The fundamental characteristics of fluidized systems were studied.[92] The fluidization of anthracite coal was shown to follow the previously established correlation for silica sands and iron Fischer-Tropsch catalyst.[93] [94] The phenomenon of channeling during a fluidization run, which occurs after bed expansion and prior to minimum fluidization of the particle bed, has been expressed in terms of a "channeling factor." It was observed that the channeling factor decreases as the average particle diameter increases; it increases as the irregularity and density of the particle increases.

## Process Development, Bench Scale

Cost estimates on Fischer-Tropsch processes, starting with coal as the source of carbon, show that a very large fraction of the cost of production of liquid fuels is the cost of synthesis-gas production and purification. It is apparent, therefore, that for industrial purposes such processes must use the synthesis gas in a very efficient manner; that is, only a minimum of gaseous hydrocarbons should be produced, and the usage ratio of hydrogen to carbon monoxide should be adjusted by selection of catalyst and operating conditions so that it is identical with the ratio in the cheapest synthesis gas.

A study of hydrogen-to-carbon monoxide usage ratios for various types of iron catalysts showed that, in the case of fused synthetic-ammonia-type catalysts, wide variations of catalyst composition and synthesis temperature caused only small changes in the usage ratio, whether the catalysts were promoted or unpromoted. Cemented and sintered or precipitated catalysts, however, showed significantly higher usage ratios in the unpromoted state. The presence of kieselguhr in precipitated

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[90] Weintraub, M., and Leva, M., Pressure Drop in Packed Tubes - A Nomogram: Chem. Eng. Prog., vol. 44, 1948, pp. 801-802.

[91] Leva, M., Fluid Flow Through Packed Beds: Chem. Eng., vol. 55, 1949, p. 115.

[92] Leva, M., Grummer, M., Weintraub, M., and Pollchik, M., Introduction to Fluidization: Chem. Eng. Prog., vol. 44, 1948, pp. 511-520.

[93] Leva, M., Grummer, M., Weintraub, M., and Pollchik, M., Fluidization of Nonvesicular Solid Particles: Chem. Eng. Prog., vol. 44, 1948, pp. 619-626.

[94] Leva, M., Weintraub, M., Grummer, M., and Pollchik, M., Fluidization of an Anthracite Coal: Ind. Eng. Chem., vol. 41, 1949, pp. 1206-1212.

catalysts leads to high-usage ratios, probably as a result of adsorption of the promoter by the catalyst support. An investigation is being made to determine the effect of synthesis-gas ratio on the usage ratio obtained with fused synthetic-ammonia type catalysts.

In addition to the oil-circulation process, a study is being made of the oil-catalyst slurry process. In the latter process, a powdered catalyst is suspended in an oil that is nonvolatile under operating conditions, and the synthesis gas is bubbled up through this suspension. In this process, the boiling range of the liquid product can be varied over wide limits by selection of catalyst and operating conditions. The oil-catalyst slurry process has the additional advantage of possible continuous removal of partly spent catalyst and continuous introduction of regenerated or fresh catalyst. Laboratory and pilot-plant work on the oil-catalyst slurry process has included a large number of tests to determine the effects of rate of gas flow and of mechanical agitation on the distribution of the catalyst powder. Earlier experiments had shown the necessity of uniform distribution of the catalyst; even a small percentage of settling in any part of the reactor results in a marked decrease in activity and durability. A study of the utility of promoted naturally occurring iron ores (for example, goethite, $FeO(OH)$) for the slurry process was also begun; a method has been developed for separating goethite from acid-soluble ferric oxide.[95]

To measure accurately the effect of the area of the gas to liquid interface, a study has been started in which a finely divided spray or fog of oil-catalyst slurry is injected into the synthesis gas. In addition to determining the importance of the gas-to-liquid interfacial area, these tests should show whether a spray or fogging type of operation is preferable to the bubbling of synthesis gas up through a column of oil-catalyst slurry.

The reduction of fused-iron catalyst is a relatively expensive step, because almost pure hydrogen is required, and the time and temperature (about 450° C.) of reduction necessitate a special installation for this operation. Precipitated catalysts can be inducted into the synthesis by treatment with synthesis gas at synthesis temperatures (about 250° C.), but this procedure has so far been found to be inapplicable to fused catalysts. Prolonged laboratory durability and activity tests are in progress to determine the effect of various degrees of reduction of iron catalysts and of impurities such as carbon oxides, methane, and water vapor in the hydrogen gas used for reduction. The results indicate that a high degree of reduction is essential for the fused iron oxide catalysts; almost complete reduction is obtained at 500° to 550° C., but the effect of pressure on the extent of reduction is less pronounced.

Carbon dioxide was shown to be about twice as effective as water vapor in decreasing the rate of reduction, whereas water vapor is more effective than carbon monoxide in this respect. At least part of the carbon monoxide and carbon dioxide is hydrogenated to methane. Methane had no effect upon reduction rate. These tests are of interest to the Demonstration Plant at Louisiana, Mo., for establishing conditions of catalyst reduction.

The unreduced fused-iron catalyst has only a very small surface area and little or no pore volume. Reduction at 450° C. provides a system of pores and fissures and

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[95] Hawk, C. O., Golumbic, N., and Hofer, L. J. E., Catalyst for Hydrocarbon Synthesis: U. S. Patent 2,449,071, Sept. 14, 1948.

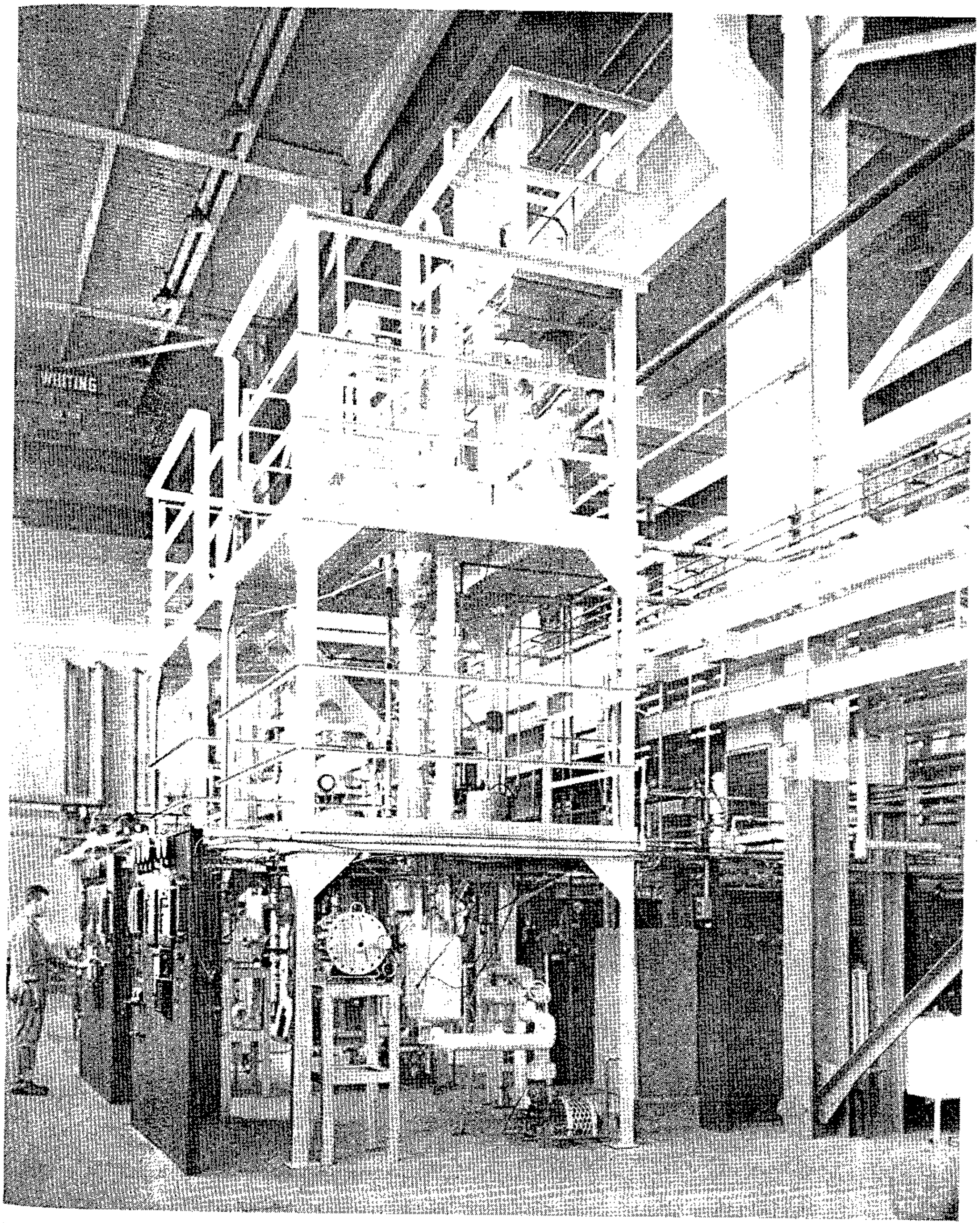

Figure 37. - Pilot plants for internally cooled (by oil circulation) process for synthesis of liquid fuels from hydrogen and carbon monoxide.

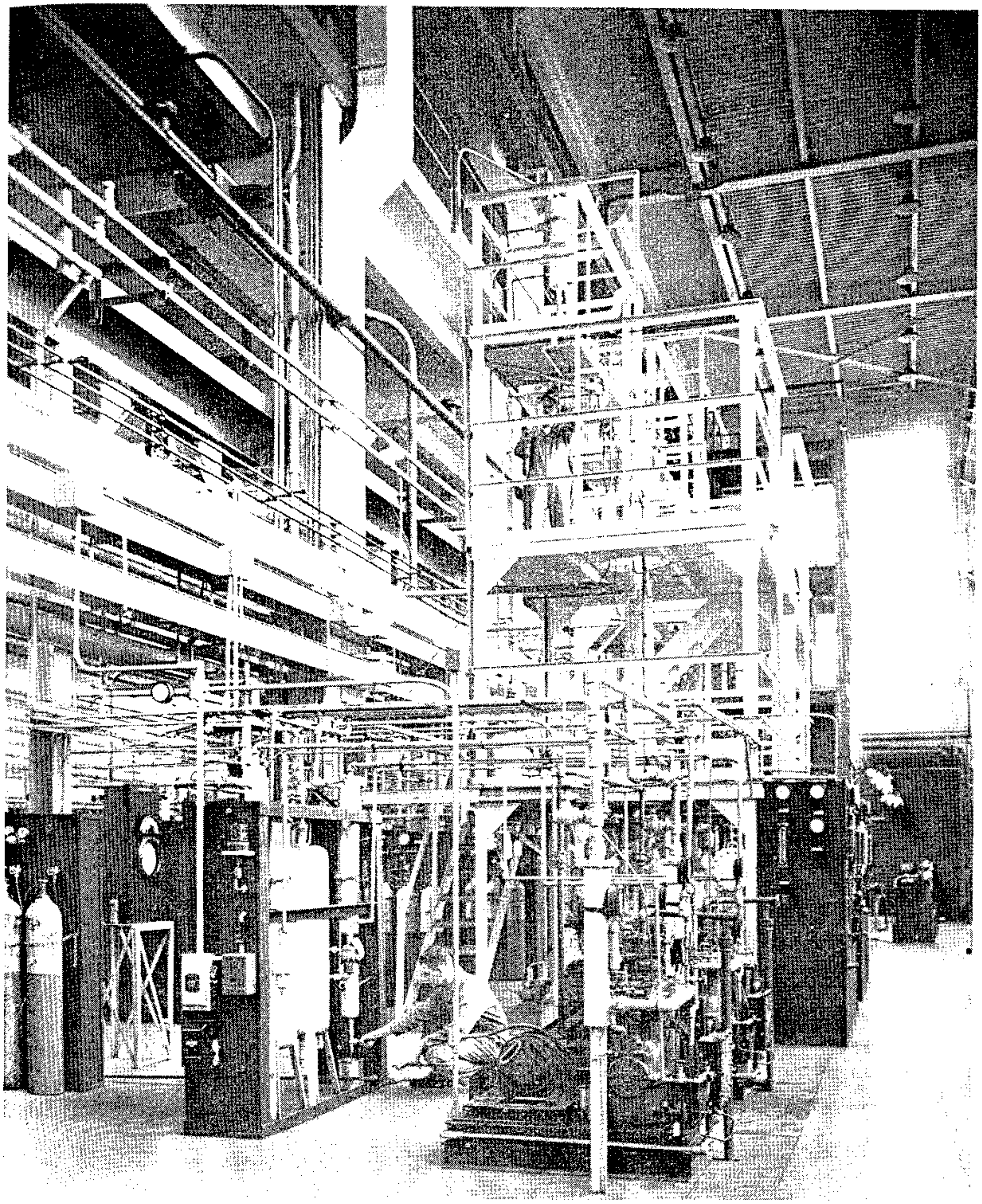

Figure 38. - Pilot plants for internally cooled (by oil circulation) process for synthesis of liquid fuels from hydrogen and carbon monoxide.

an increased surface area. The unreduced precipitated catalysts have a relatively large area and pore volume and do not need extensive reduction before use in the synthesis. The sintered catalysts prepared from iron ores or mill scale resemble the fused catalysts, so far as reduction is concerned. However, the induction of a promoted goethite ore catalyst in synthesis gas at 325° C. has been found to result in a catalyst nearly as active as one reduced in hydrogen. Laboratory experiments are continuing this work.

## Process Development, Pilot-plant Operations

A duPont synthetic-ammonia fused-iron catalyst was operated for about 3 months in the Fischer-Tropsch synthesis in the internally cooled (by oil circulation) process that uses a completely flooded bed of granular catalyst. The pilot plants are shown in figures 37 and 38. Operation was finally discontinued because of excessively high pressure drop across the catalyst bed. The operating temperature at this time was 269° C. for a carbon dioxide-free contraction of 59 percent. Treatment of the catalyst with hydrogen did not reduce the pressure drop through the bed, nor could the low temperature (255° C.) achieved in the early part of the synthesis be duplicated.

The second internally cooled converter was placed in operation, and these two units were used to study the effect of catalyst grain size and synthesis gas composition. Fused-iron catalyst of 2 to 4 mesh required an operating temperature of 272° C., compared to 255° C. required when 4- to 6-mesh catalyst was used. The addition of carbon dioxide to the fresh synthesis gas, the purpose of which was to simulate an unscrubbed synthesis gas prepared from coal, showed that carbon dioxide had no effect other than as a diluent. The use of hydrogen-rich synthesis gas, however, decreased not only the formation of acid in the converter but also the production of the heavier oils in favor of lighter hydrocarbons.

Because of the difficulties encountered in plugging the catalyst in the internally cooled converter, it was decided to try a modification of this design in which the catalyst is lifted by increased liquid velocity and kept suspended in a stream of liquid and gas. This design has been designated as a "moving-bed" converter. The result of preliminary work with this unit has shown that, as compared to fixed-bed operation, the moving-bed technique has the following advantages: (1) Greater space-time-yield, based on catalyst bed or converter height; (2) greater product yield on the basis of pounds of product per pound of catalyst; (3) elimination of the cementing of catalysts and large pressure drops; and (4) the possibility of treating the catalyst continuously with hydrogen in a side stream, should this be desired.

## Separation and Identification of Products of Hydrogenation of Carbon Monoxide

Detailed characterization of the Fischer-Tropsch products obtained from iron catalysts is in progress. The determination of the oxygenated compounds in Fischer-Tropsch products by infrared spectrometry has been facilitated by the derivation of absorption coefficients for the functional groups of alcohols, ketones, aldehydes, esters, and acids in mixtures with hydrocarbons. This has minimized the previous requirements that pure calibration compounds be available. Thus, the limitations due to differences in molecular weight and density have been reduced, and calibrations based on the simpler $C_4$ oxygenated compounds can now be used to analyze oxygenated