

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

The work of the Coal-to-Oil laboratories and Pilot Plants during the calendar year 1949 has been concerned chiefly with the development of new or improved processes related to the production of liquid fuels from coal. This work may be divided into two broad categories: (1) The synthesis of liquid fuels from the gasification products of coal - hydrogen and carbon monoxide - by the Fischer-Tropsch and related processes, and (2) the direct hydrogenation of coal by the Bergius process.

Synthesis of Liquid Fuels from Hydrogen and Carbon Monoxide

Process Development

Pilot-Plant Operations

Operation of the internally cooled (by oil circulation) process, which uses a completely flooded bed of granular iron catalyst, was continued in pilot-plant studies of catalyst durability and product distribution. A duPont synthetic-ammonia-type catalyst (doubly promoted with potassium and magnesium oxides) was operated for about 3 months in the Fischer-Tropsch synthesis, at the end of which time the operating temperature was 260° C. for a carbon dioxide-free contraction of 59 percent. Operation was discontinued because of excessively high pressure drop across the catalyst bed. Treatment of the catalyst with hydrogen did not decrease the pressure drop through the bed, nor could the low temperature (255° C.) of the early part of the synthesis be obtained.

Two pilot-plant 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 about 10 percent of carbon dioxide to the fresh synthesis gas, the purpose of which was to simulate an unscrubbed synthesis gas prepared from coal, showed that this proportion of carbon dioxide had no effect other than that of 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 by cementing of the catalyst grains in the internally cooled converter, it was decided to try a modification of this design in which the catalyst is lifted by an 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 or on pounds of product per pound of catalyst; (2) elimination of the cementing of catalysts and of large pressure drops; and (3) treatment of the catalyst with hydrogen continuously in a side stream, should this be desired. The gases in the converter system were shown to be increasingly soluble in the circulating oil in the following order: Hydrogen, carbon monoxide, and carbon dioxide. A conversion about 65 percent as great was obtained by introducing the synthesis gas into the free space at the top of the converter as was obtained by bubbling the gas up through the converter in the conventional method. This experiment shows that diffusion of the reactants to the catalyst surface is not the rate controlling step in the process.

Current pilot-plant operations are being oriented to determine the conditions for minimum production of gaseous hydrocarbons and to study the feasibility of

conducting the synthesis in two stages without removal of carbon dioxide between stages.

Laboratory-Scale Experiments

Catalysts. - The development of cheap, durable, and adequately active catalysts for the internally cooled, oil-circulation process was continued. Alkali-impregnated glomerules made from iron oxide powder 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.

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 drastically modified by heat. In the present catalyst, the particles of iron oxide are cemented into granules by the borax, and no drastic change is considered as taking place.

Work has continued on duplication of the German synol catalyst ($\text{Fe-Al}_2\text{O}_3\text{-CaO-K}_2\text{O-SiO}_2$), which was found to be much more active than the usual synthetic-ammonia-type catalysts, comparing favorably 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 enhanced 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.

On the basis of a series of tests with commercial synthetic-ammonia-type catalysts, calculations were made, assuming spherical particles, which indicated that, of the catalyst surface, only a depth of about 0.1 mm. is effective in the synthesis. This implies that a catalyst with a system of pores large enough so that their surface area may be regarded as external area should have a greater activity than the fused catalysts. Large variations of activity with particle size are seldom observed in most catalytic systems, especially those in which both products and reactants are gaseous. For example, it has been shown that the rate of ammonia synthesis on fused-iron catalysts was independent of particle size. However, in the Fischer-Tropsch synthesis, the catalyst pores are probably quite completely filled with hydrocarbons that are liquids at synthesis temperatures, and this may account for the dependence of rate on particle size.

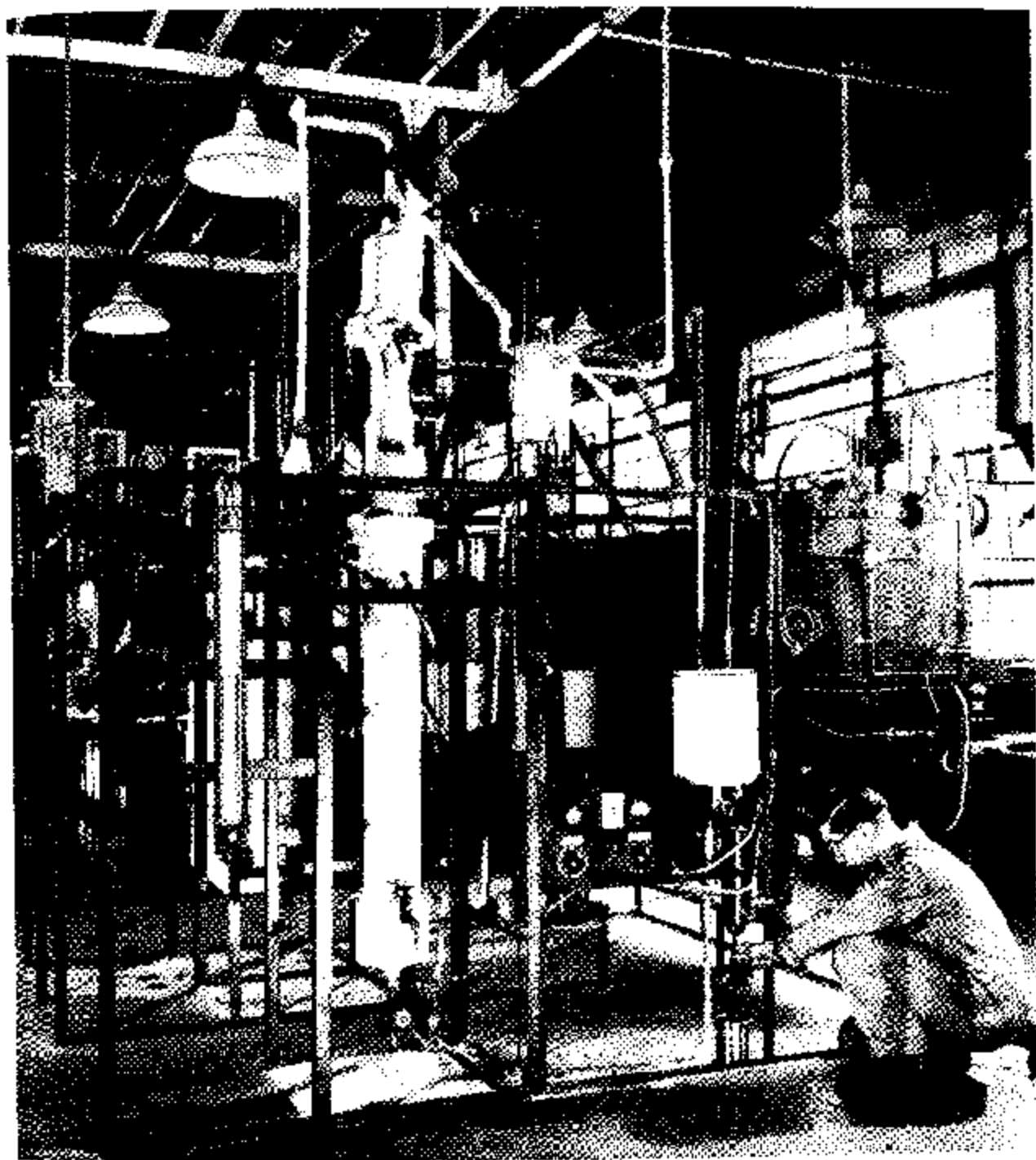


Figure 33. - Static-bed slurry unit for hydrocarbon synthesis.

Of the materials used in promoting iron catalysts, variation of the concentration of alkali appears to cause the greatest change in activity and product distribution, but much of the evidence reported in the literature is contradictory. As the result of tests with cemented, precipitated, and fused-iron catalysts, an alkali content of 0.4 to 0.6 part of K_2O per 100 parts of iron was found to be the optimum for promoting catalyst activity. The results of these tests can be explained by assuming that the presence of alkali increases not only the rate of carbide formation, which is essential to high catalyst activity, but also the rate of free-carbon deposition, which is detrimental to catalyst activity. The acid content of the products also increases with alkali content of the catalyst, and the organic acids so formed may be instrumental in deterioration of the catalyst. Catalysts of high alkali content are mechanically unstable. No significant conclusions could be drawn concerning the product distribution of alkali-promoted fused and cemented catalysts, because the observed increase in the proportion of higher-molecular-weight products may have been a natural result of the decreased operating temperature, which was possible by virtue of the increased activity of the promoted catalyst. Precipitated-iron catalysts, however, showed smaller differences in activity than the other types of catalyst, and the resulting operating temperature was not considered low enough to account for the increase in molecular weight of the product. It is concluded, therefore, that an increase in alkali content of the catalyst tends to increase the average molecular weight of the products.

An investigation of the hydrogen:carbon monoxide usage ratios obtained over different types of iron catalysts was made to improve the efficiency of the conversion of synthesis gas, the production and purification of which constitute a large fraction of the total cost of producing liquid fuels from coal by the Fischer-Tropsch process. The results show that, in the case of fused synthetic-ammonia-type catalysts, wide variations of catalyst composition and synthesis temperature cause only small changes in the usage ratio, whether the catalysts are promoted or unpromoted. Cemented and sintered or precipitated catalysts, however, show significantly higher usage ratios in the unpromoted state. The presence of kieselguhr in precipitated 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.

A study was begun on the utility of promoted naturally occurring ores for the oil-catalyst slurry process. In this process, a powdered catalyst is suspended in an oil that is nonvolatile under operating conditions, and the synthesis gas is bubbled up through the suspension. An example of such an ore is goethite [$\alpha\text{-FeO(OH)}$], and a method for separating it from acid-soluble ferric oxide has been developed. 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 ore reduced in hydrogen.

Because of the inherent mechanical difficulties encountered in operating a circulating-slurry unit using precipitated-iron catalysts, a static-bed type of reactor (see Fig. 33) has been constructed which does not involve circulation outside of the reactor. Synthesis gas enters at the bottom through a conical distributor, and reactor oil is separated from the catalyst by a porous metal filter in the upper section. Experiments concerning the effect of induction procedures on catalyst activity, which were carried out in this unit, showed that induction of precipitated-iron catalysts at atmospheric pressure leads to a higher catalyst activity and a higher $H_2:CO$ usage ratio.

Catalyst Reduction. - Investigation of the effect of temperature, pressure, and gas composition on the extent of reduction of iron catalysts showed that 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, while 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 which, itself, has no effect on reduction rate. Reduction of an iron synthetic-ammonia-type catalyst with hydrogen from which all oxygen had been removed showed that the small amount of oxygen usually contaminating commercial hydrogen does not hinder reduction of this catalyst.

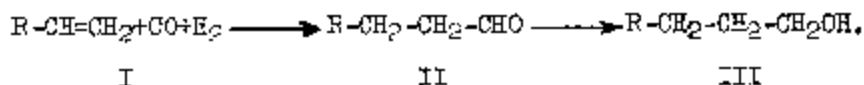
Refining of Fischer-Tropsch Gasoline. - A fixed-bed gas-phase unit (see fig. 34) was adapted for use in a process to convert oxygenated compounds in Fischer-Tropsch product oil to hydrocarbons and water by dehydration over activated alumina. Reforming also takes place, resulting in a shift of the olefin linkage. Preliminary experiments showed the optimum conditions to be a temperature of 350° C. and a liquid-space velocity of 1 volume of oil per volume of catalyst per hour; almost complete removal of all oxygenated compounds was observed, along with the production of considerable ethylene and propylene, chiefly by dehydration of ethanol and propanol.

Heat Transfer in Fluidized Catalyst Beds and Pressure Drop in Granular Beds. - In connection with a determination of the fundamental properties of fixed and 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. In the particle-size range 0.0015 to 0.0180 inch, the heat-transfer coefficient was found proportional to the product of the specific heat, thermal conductivity, and mass velocity of the gas and to the efficiency of fluidization (fluidization work divided by the fluidization work plus the bed expansion work). It was also found inversely proportional to the composite diameter of the particle and proportional to the modified Reynolds number raised to the 0.45 power. A nomograph has been completed for calculating 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 are necessary through packed tubes.

The OXO Reaction: Homologation of Alcohols

A study is in progress of the mechanism of the addition of hydrogen and carbon monoxide to olefins (known as the "OXO" reaction) to produce aldehydes, ketones, and alcohols. This reaction occurs to some extent during the synthesis of hydrocarbons and alcohols by the Fischer-Tropsch process. A more complete knowledge of the mechanism of the OXO reaction is essential in further development of the Fischer-Tropsch process.

The usual OXO reaction consists of the reaction of an olefin to produce the next higher alcohol according to the scheme:



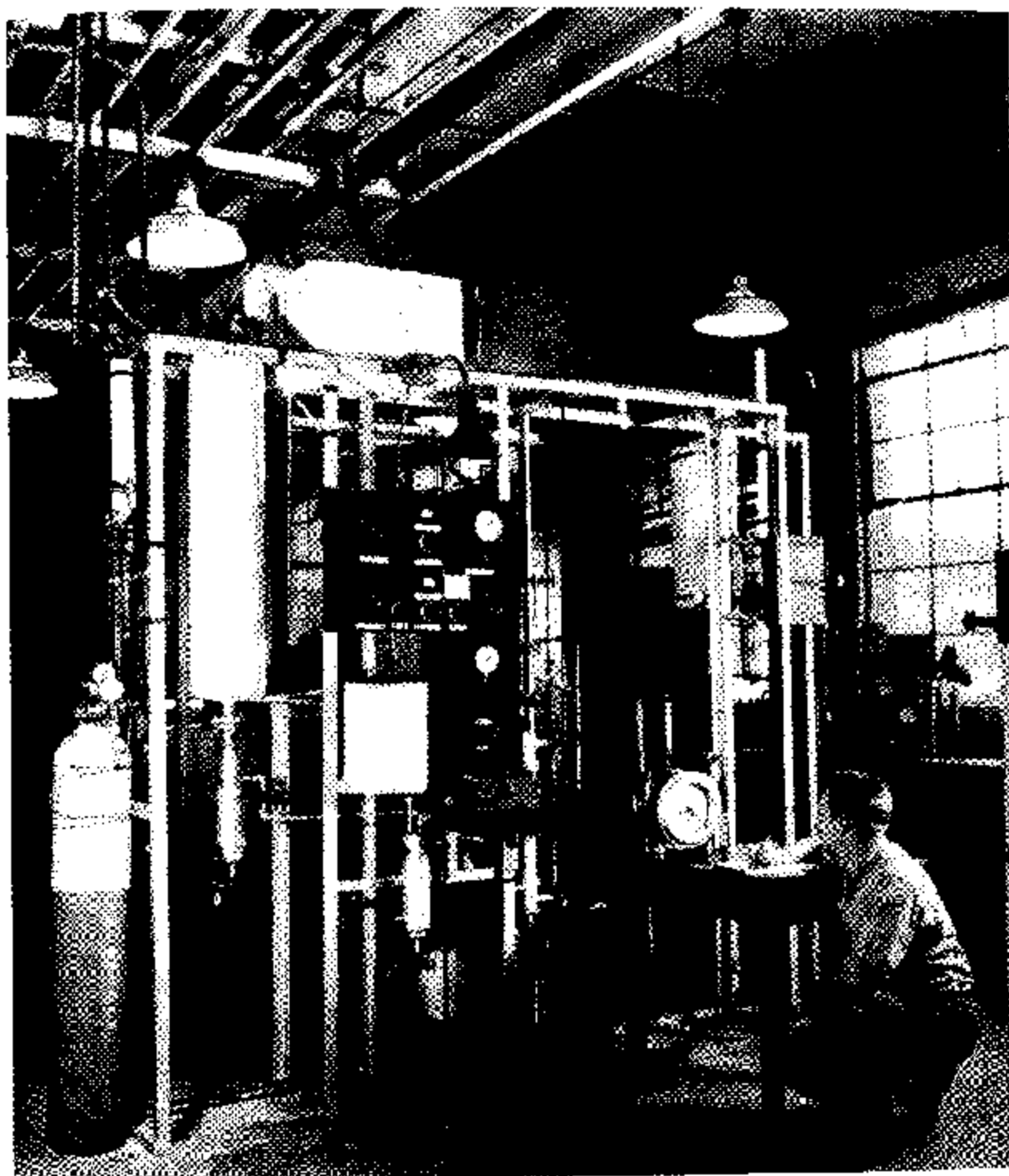
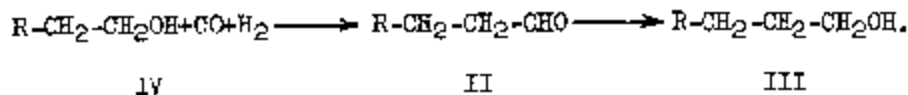


Figure 34. - Product-reforming unit for ungrading gasoline.

It has been found that, under the conditions (200-300 atmospheres, 160°-200° C.) of the OXO reaction, if an alcohol is used as a starting compound in place of the usual olefin, the final product consists of the homologous alcohol; that is, the alcohol containing one more carbon atom than the starting alcohol. The homologation reaction can be written:



The most obvious explanation of the homologation reaction consists in the assumption that the alcohol (IV) first loses water to give (I), which then proceeds to react according to the usual OXO reaction to give compound (III). This may be the explanation in certain cases, but evidence exists that the homologation does not proceed via an olefin intermediate. Instead, it is thought that the synthesis may occur via a hypothetical ionic intermediate which would explain the known formation of acids and esters. This scheme postulates that the reaction is homogeneous and catalyzed by the acid, cobalt hydrocarbonyl.

The homologation reaction has tremendous commercial significance. The conversion of one alcohol to the homologous alcohol is usually a tedious and arduous synthetic process. The reaction has important implications for the mechanism of the Fischer-Tropsch process as well. It is known that the OXO reaction occurs to a limited extent under certain conditions of operation of the Fischer-Tropsch process. If conditions (catalyst, temperature) can be found such that the alcohol homologation reaction is sufficiently rapid at pressures of not more than about 70 atmospheres, it may well replace the Fischer-Tropsch synthesis as a source of liquid fuels. The C₃ to C₁₀ alcohols could be converted to olefinic hydrocarbons by passage over bauxite at about 300° C., and the C₁₀+ cracked and recycled. The advantages of such a process would be: (1) The synthesis gas need not be purified because the OXO reaction is not greatly retarded by sulfur compounds, and (2) the OXO reaction is a homogeneous catalytic reaction, and preparation of special contact catalysts would not be necessary.

Iron Catalysts and the Fischer-Tropsch Synthesis

Nitrided Catalysts

The deposition of carbon in Fischer-Tropsch catalysts is deleterious to their activity and durability. This is especially serious in the hot-gas-recycle and the fluidized-iron processes. The carbon is formed by the reaction: $2\text{CO} = \text{CO}_2 + \text{C}$. For some time, physical chemists in the synthetic liquid fuels research and development laboratories have considered it probable that the carbon-forming reaction proceeds in several steps, one of which is the formation and decomposition of iron carbides. In accord with this view, carbon formation should be eliminated or at least its rate greatly reduced by substituting, for the iron carbide, materials such as iron boride or iron nitride whose lattice structure is similar to that of the carbide.

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 depending upon the temperature, time, space velocity of ammonia, and the ammonia:hydrogen ratio. Accordingly, fused-iron synthetic-ammonia-type catalysts were reduced in hydrogen at 450°-550° C. and nitrided at 350°-385° C. These nitrides of iron are interstitial compounds similar to the carbides of iron, normally formed when iron catalysts are used in the Fischer-Tropsch synthesis.