

PART I - OIL FROM COAL

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

Among the highlights of laboratory and pilot-plant work at Bruceton, Pa., on producing liquid fuels from coal by gas synthesis were: Restoration of spent Fischer-Tropsch catalysts (steel turnings) by injection of an alcoholic solution of potassium hydroxide into the reactor; studies of pretreating and activating such novel catalysts as steel wool and alloy steels; development of a method for reducing finely divided slurry catalysts in a dry, fixed-bed reactor; and pilot-plant confirmation that the hot-carbonate process for removing carbon dioxide from synthesis gas offers substantial savings compared with conventional methods.

In coal hydrogenation, the one-step, high-temperature process was tested in a continuous pilot plant and gave nearly complete conversion of coal to oil, but yields of gasoline and gaseous hydrocarbons were relatively low. Carbohydrates, cellulose, and lignin were heated or treated with acid to produce coallike chars that can be hydrogenated to products typical of coal hydrogenation to obtain additional information about the formation reactions of coal. Further advances were made in developing analytical methods, and studies were started on microbial degradation of coal and on the kinetics of the reactions of carbon with carbon dioxide and steam.

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

Process Development

Pilot-Plant Operations

Oil-Circulation Process. - Synthesis of oil from mixtures of hydrogen and carbon monoxide (synthesis gas) takes place in the presence of catalysts and can be accomplished in a number of ways. In the oil-circulation process, the catalyst is completely submerged in oil, and heat given off during reaction is carried off as sensible heat of the liquid. Last year, particularly durable catalysts developed for this process were mentioned; they consist of specially activated lathe turnings of iron and steel.

Two pilot-plant tests now have been made with turnings pretreated by oxidation, reduction, carburization, and reoxidation to improve activity and longevity by operating at temperatures below 270° C. Carburization converts metallic iron to iron carbides and deposits carbon on the surface by decomposition of carbon monoxide. Reoxidation with steam converts carbides to oxides and removes some free carbon. In laboratory tests, this pretreatment had produced catalysts of high activity. In the plant, however, pretreatment was difficult, and no increased activity was observed. Flowing oil gradually removed the soft coating of the catalyst by hydraulic attrition. With conventionally prepared turnings, operations lasted 2,700 hours under severe oxidizing conditions at temperatures as high as 292° C. With carburized turnings the experiment had to be terminated after 1,530 hours even though the temperature never exceeded 275° C.

Doubly oxidized-reduced turnings also were tried. They were oxidized with steam until 20 percent of the iron was converted to magnetite. Subsequent reduction with hydrogen was followed by a second oxidation with steam, impregnation with alkali, and a second reduction with hydrogen. This preparation was no more active than conventionally prepared turnings.

Injection of alkali had the same effect on product distribution from lathe turnings as from other iron preparations. After 1,100 hours of operation, production of  $C_1+C_2$  gases had increased from 28 to 63 grams per cubic meter of synthesis gas converted, wax had decreased from 16 to 1.7 percent of  $C_3^+$  material, and production of gasoline had risen from 40 percent to 86. This shift was evidence of loss of alkali from the catalyst surface. When alcoholic potassium hydroxide was injected with the recycle oil, normal distribution of products was restored immediately.

Samples of the surface layers of turnings taken during synthesis showed that Hägg iron carbide (indicated as " $Fe_2C$ ") was produced early in the synthesis; its amount remained fairly constant, while metallic iron was gradually oxidized to magnetite (see fig. 4).

Removal of Carbon Dioxide From Synthesis Gas. - In the Fischer-Tropsch synthesis, removal of carbon dioxide from synthesis gas is a necessary and relatively costly step. In the ethanolemine process, the best available method, steam costs are 2 to 3 cents per gallon of liquid fuel. A purification process is being developed in which amine is replaced by a hot, concentrated solution of potassium carbonate at elevated pressure. As absorption of carbon dioxide takes place at the same temperature as regeneration of the solution, the amount of steam required for regeneration is reduced, and the need for expensive heat exchangers is eliminated. The pilot plant for this process was described in the 1953 Annual Report.

Studies have been completed of the effect of operating variables upon regeneration efficiency. Regeneration efficiency is a measure of the amount of steam required for regenerating the spent solution and is expressed as cubic feet of carbon dioxide per pound of steam. Feed gases containing 10, 16, 20, and 30 percent carbon dioxide (remainder nitrogen) were used at absorber pressures of 100 to 400 p.s.i.g. Residual carbon dioxide in scrubbed gas was varied from 0.5 to 6 percent. Tests were made with single-stream and split-stream flow of regenerated carbonate. In split-stream operation about one-third of the solution was cooled  $20^\circ C$ . and sent to the top of the absorber; the main portion was not cooled and entered 5 feet below the top of the absorber. Split-stream operation was particularly advantageous when the desired concentration of carbon dioxide in scrubbed gas was less than 1 percent.

Variables that affected regeneration efficiency were partial pressures of carbon dioxide in the raw and scrubbed gases, pressure of regeneration, and amount of carbon dioxide absorbed by the solution. The regeneration efficiency (see fig. 5) rose sharply with increasing partial pressure of carbon dioxide in the raw gas up to about 45 p.s.i.g. and then leveled off. Similar results were obtained with single streams. From figure 5 one can predict the regeneration efficiency for a given feed gas.

Optimum removal of carbon dioxide and regeneration efficiencies obtained with several gas compositions are given in table 1. The process was compared with amine scrubbing, with a gas at 300 p.s.i.g. scrubbed from 16 to 2 percent carbon dioxide, to illustrate savings in steam consumption. For split-stream flow a maximum regeneration efficiency of 9.8 was attained (table 1). In commercial practice with a 15- to 20-percent solution of monoethanolamine, the regeneration efficiency is about 3.0 to 4.0.

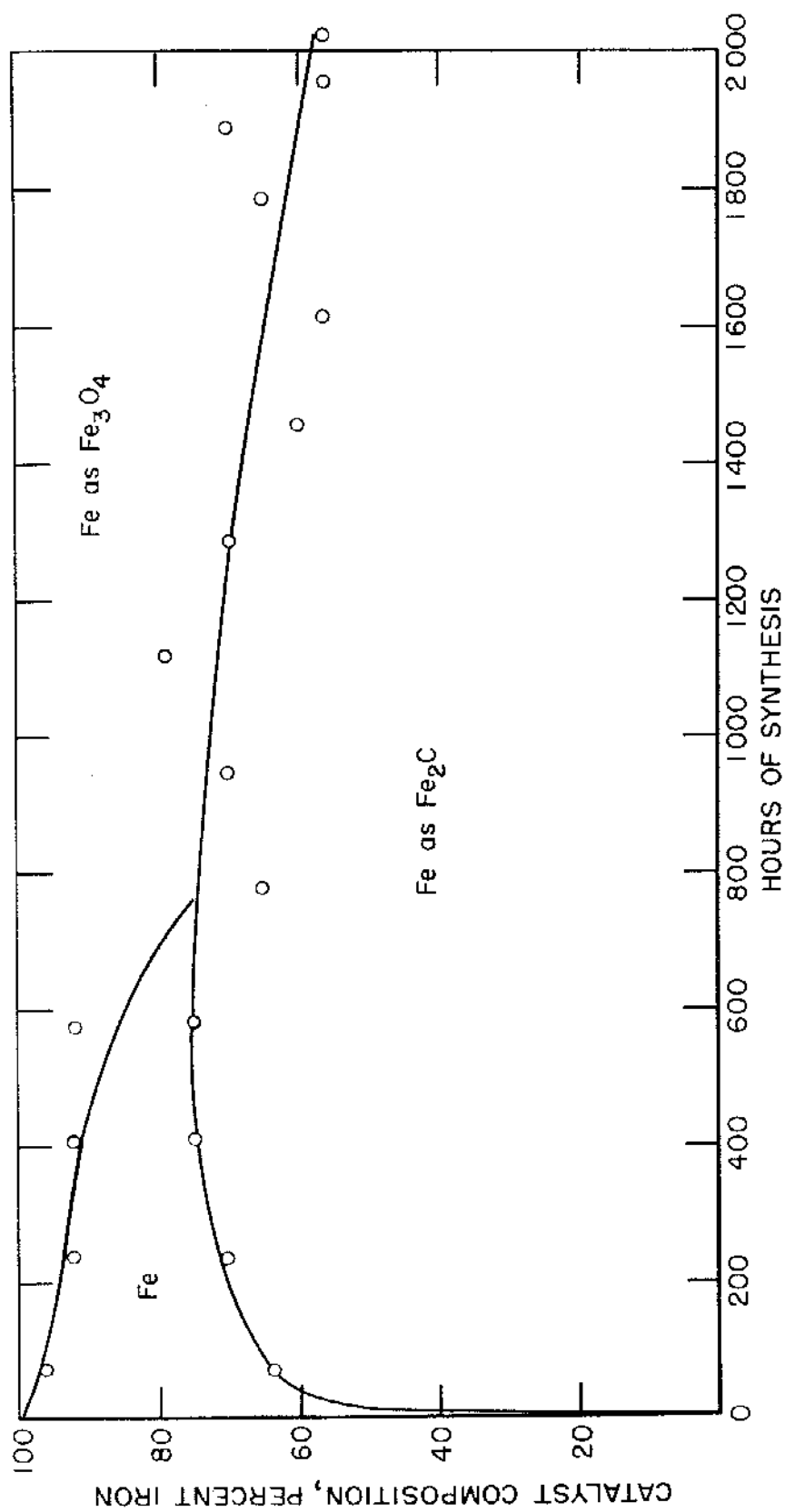


Figure 4. - Change in composition of surface of lathe turnings during Fischer-Tropsch synthesis.

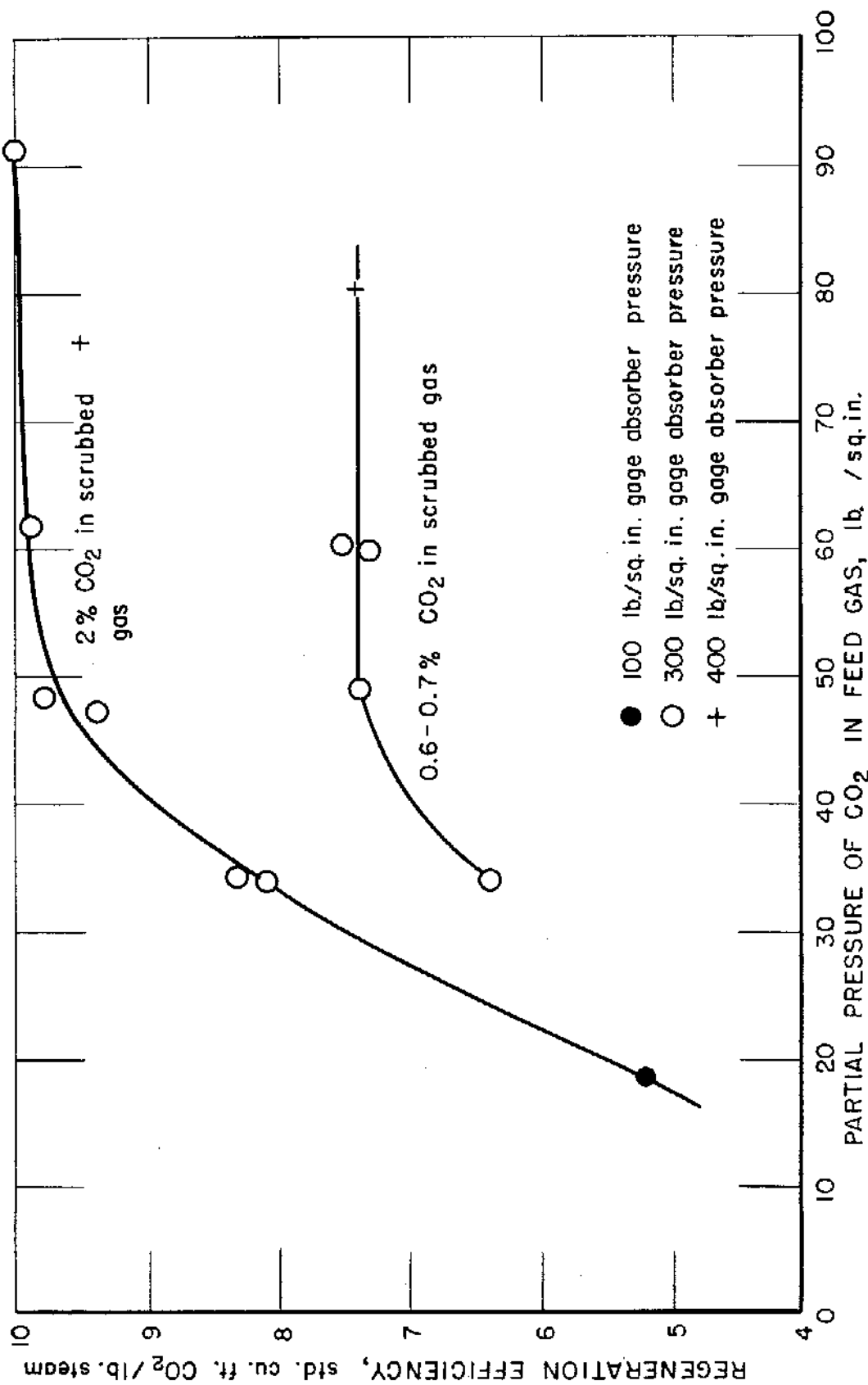


Figure 5. - Removal of carbon dioxide from synthesis gas by potassium carbonate solutions. Effect of partial pressure of CO<sub>2</sub> in the feed gas on regeneration efficiency (split stream).

TABLE 1. - Optimum operating conditions for removing carbon dioxide from synthesis gas by potassium carbonate solutions

(300 p.s.i.g. absorber pressure, 2 to 4 p.s.i.g. regenerator pressure)

| CO <sub>2</sub> content, percent |              | Single stream                       |  | Split stream                        |  |
|----------------------------------|--------------|-------------------------------------|--|-------------------------------------|--|
| Feed gas                         | Scrubbed gas | CO <sub>2</sub> pickup, cu.ft./gal. | Regeneration efficiency, cu.ft. CO <sub>2</sub> /lb. steam | CO <sub>2</sub> pickup, cu.ft./gal. | Regeneration efficiency, cu.ft. CO <sub>2</sub> /lb. steam |
| 20                               | 2            | 3.8                                 | 9.4  | 3.8                                 | 9.8  |
| 20                               | .8           | 4.5                                 | 6.8  | 4.0                                 | 7.8  |
| 20                               | .6           | -                                   | -  | 4.2                                 | 7.5  |
| 16                               | 2            | 3.7                                 | 8.5  | 3.4                                 | 9.8  |
| 16                               | .8           | 3.7                                 | 6.05   | 3.8                                 | 7.7  |
| 16                               | .6           | -                                   | -  | 3.9                                 | 7.3  |
| 10                               | 2            | -                                   | -  | 3.1                                 | 8.3  |
| 10                               | .6           | -                                   | -  | 3.1                                 | 6.0  |

Investigation of simultaneous removal of carbon dioxide and hydrogen sulfide has been started. About 93 percent of the hydrogen sulfide was removed (concentration lowered from 0.77 to 0.06 percent) when the concentration of carbon dioxide was reduced from 11 percent to 2. An additional reduction of hydrogen sulfide was attained when the concentration of carbon dioxide was decreased further.

#### Bench-Scale Experiments

Catalyst-Oil Slurry Process. - The slurry process also utilizes oil as an internal coolant. It differs from the oil-circulation process in that the catalyst particles are small enough so that they can be suspended in the oil. Evaluation of magnetite and fused-iron catalysts was continued, particularly factors that result in operational difficulties such as agglomeration and settling of suspended particles. The problem has been attacked mechanically, chemically, and process-wise.

Reactor design was aimed at increasing the flow of slurry by providing enough agitation to prevent agglomeration. In 1 design, 2 tubes were arranged concentrically so that incoming gas passed up the central tube and carried slurry as in a gas lift. The slurry then returned to the bottom of the reactor through the annular space. Some satisfactory tests were made with this arrangement. Another system, just built, employs a turbine-type pump that circulates slurry through an external section that may serve as a heat exchanger. Here too, an appreciable shearing force should prevent agglomeration. The system can be operated with countercurrent gas and slurry flows.

Some factors that may affect agglomeration are viscosity and composition of suspension oil. Tests with oils of high viscosity were unsuccessful and suggest that some colloidal phenomenon, such as adsorption or peptization, may cause trouble. When a high-molecular-weight aliphatic alcohol (dodecyl alcohol) was added, much longer runs were obtained; the reason for this effect is being studied.

A method was developed for reducing finely divided catalysts in the dry state by passing hydrogen over a layer of catalyst in a horizontal reactor. This procedure has definite advantages over reduction of the catalyst in oil. The minimum temperature was found to be 325° C.

## Catalyst-Testing Studies

Steel Lathe Turnings

Multiple Oxidations and Effect of Oxidation Temperature. - The effect of multiple oxidations and reductions of 1,018 carbon-steel turnings on catalytic activity was studied. In each instance, only about 20 percent of the iron was oxidized with steam. The catalyst was impregnated with alkali before final reduction. Activity coefficients ( $A_{Fe}$ ) of 68, 74, and 48 were obtained for single, double, and triple oxidation, respectively, where  $A_{Fe}$  is the volume of  $H_2 + CO$  (in cubic centimeters) that would have reacted per gram of iron per hour at  $240^\circ C$ . The triply oxidized catalyst produced larger amounts of wax than the others and gave higher yields of olefins in the  $C_2-C_4$  fraction. At first, doubly oxidized turnings appeared to be appreciably more active than singly oxidized ones. However, the differences were due chiefly to different bulk densities of the two samples; the activity per gram of iron was essentially the same.

The effect of temperature of oxidation on activity and selectivity of the turnings was determined up to  $800^\circ C$ . In 1 test, the temperature was increased from  $100^\circ$  to  $600^\circ C$ . over a 10-hour period and then held at  $600^\circ C$ . for 30 hours. In another, the catalyst was oxidized at  $600^\circ C$ . for 32 hours and in a third at  $800^\circ C$ . for 1-1/2 hours. In all instances, the extent of oxidation was approximately 20 percent. Each catalyst charge was alkalinized with 2-percent potassium carbonate solution and given the standard reduction with hydrogen. Synthesis tests were made for 6 weeks at 300 p.s.i.g. with  $H_2 + CO$ . Activity values ranged from 57 ( $600^\circ C$ . oxidation) to 77 ( $800^\circ C$ .). The  $100^\circ$  to  $600^\circ C$ . oxidation that is currently used resulted in an activity of 68. The rate of oxidation of steel turnings depended on the temperature. At  $875^\circ C$ ., oxidation was a linear function of time. At lower temperatures the rates were constant only initially. At  $575^\circ C$ ., oxidation virtually stopped after about 18 to 20 percent of the iron had been affected. For thorough oxidation, the temperature must be considerably higher than  $575^\circ C$ .

Composition Tests. - Activity tests on lathe turnings prepared from various types of steels and alloys are in progress. Turnings of Armco iron (1018, 1042, 1095, 1340 carbon steels) and 2-percent copper steel were oxidized with steam to about 20 percent, alkalinized with 2-percent potassium carbonate solution, and reduced with hydrogen at  $450^\circ C$ . for 8 hours at an hourly space velocity of 1,000. The copper-steel alloy was most active ( $A_{Fe}$  of 84). The largest percentage of products in the gasoline range (52 percent of total product) was obtained with 1018 carbon-steel. Product distributions from the remaining tests were quite similar.

Pretreatment of Steel Turnings. - Efforts are being made to improve the activity and selectivity of 1018 carbon-steel turnings by pretreating the oxidized turnings before addition of alkali and final reduction. These pretreatments are: Nitriding with ammonia, carburizing with synthesis gas, and impregnation with 1 percent copper oxide. One of the first pretreatments consisted of: (a) Oxidation with steam at  $600^\circ C$ ., (b) reduction with hydrogen at  $450^\circ C$ ., (c) carburization with  $H_2 + CO$  at  $450^\circ C$ ., (d) reoxidation with steam at  $600^\circ C$ ., (e) impregnation with 2-percent potassium carbonate solution, and (f) reduction with hydrogen at  $450^\circ C$ .

Operating conditions for the comparative tests were: Pressure 300 p.s.i.g., hourly space velocity of  $H_2 + CO$  300, with the temperature adjusted to maintain 65-percent carbon dioxide-free contraction. This particular catalyst was operated in synthesis for 13 weeks and had an activity coefficient of 98 at an average temperature of  $254^\circ C$ . for the first 6 weeks, the period used for comparative purposes.

Oxidized, alkalized, and reduced 1018 turnings had a lower activity of 68 and operated at 263° C. for the first 6 weeks. The only significant difference in selectivity was that the carburized turnings produced 18 percent wax, based on total hydrocarbon yield, the uncarburized material only 4 percent. With the increase in wax, there was a proportionate decrease in other fractions that was divided fairly equally.

In another test the same procedure was followed, except that the second oxidation and reduction were omitted. This sample had an activity of only 28. The surface layer was essentially cementite ( $\text{Fe}_3\text{C}$ ); reoxidation destroys this carbide. As the reoxidized catalyst was more active than the carbide, either the carbide may be assumed to be relatively inactive, or structural changes produced by oxidizing the carbide (greater porosity, higher surface area) are mainly responsible for greater activity. The selectivity of these two catalysts was similar, despite a large difference in operating temperature.

Another batch of turnings was oxidized 20 percent with steam, impregnated with potassium carbonate solution (0.039 percent potassium oxide on turnings), reduced with hydrogen, and nitrided with ammonia at 350° C. for 16 hours at an hourly space velocity of 1,000. The nitrogen-iron ratio, based on weight gain, for the nitrided catalyst was 0.099. X-ray diffraction showed the presence of hexagonal iron nitride. The test was terminated voluntarily after 6 weeks when the catalyst was discharged and analyzed. Nitrided turnings were less active than oxidized-reduced turnings (A<sub>Fe</sub> 55 and 68, respectively) and produced larger amounts of C<sub>1</sub> to C<sub>4</sub> hydrocarbons (52 and 27 percent) and very small amounts of heavier hydrocarbons (5 and 10 percent). Spectrometric analyses showed high yields of alcohols and oxygenates in the oil and water layers. The used catalyst was extracted with toluene to remove hydrocarbons and then shaken vigorously for 3 hours to crack off the active surface. X-ray diffraction showed that this surface was hexagonal iron carbonitride.

Pretreatment of steel turnings, involving carburization or nitriding followed by oxidation and reduction, produced significant increases in porosity and surface area with a corresponding increase in activity. For surface areas from about 0.3 to 1.5 square meters per gram, the activity increased approximately linearly with surface area.

The 1018 carbon-steel turnings were also impregnated with 1 percent copper oxide. The treatment consisted of: (a) Oxidation with steam at 600° C., (b) impregnation with about 1 percent copper oxide by immersion in a copper nitrate solution and subsequent heating to decompose the nitrate, (c) alkalization with a solution of 2 percent potassium carbonate, and (d) reduction with hydrogen at 450° C. This catalyst had a high activity of 110 and satisfactory selectivity. On the basis of synthesis data and simplicity of preparation and pretreatment, copper-impregnated turnings at present appear to be the most attractive catalyst of this type.

#### Fused Promoted Magnetite

Boriding Studies. - Catalysts containing borides of iron apparently have not been made as yet. To obtain such compounds, diborane ( $\text{B}_2\text{H}_6$ ) was prepared in an all-glass-apparatus (see fig. 6) by slow addition of boron trifluoride ethyl etherate to an agitated suspension of lithium hydride in diethyl ether. The purified gas was kept in a storage bulb. Because of the explosive properties of diborane, strict precautions were taken to eliminate traces of air and moisture in the apparatus.

A 20- to 30-percent mixture of diborane in helium was passed through both reduced and nitrided iron to determine whether borides would form. Helium was

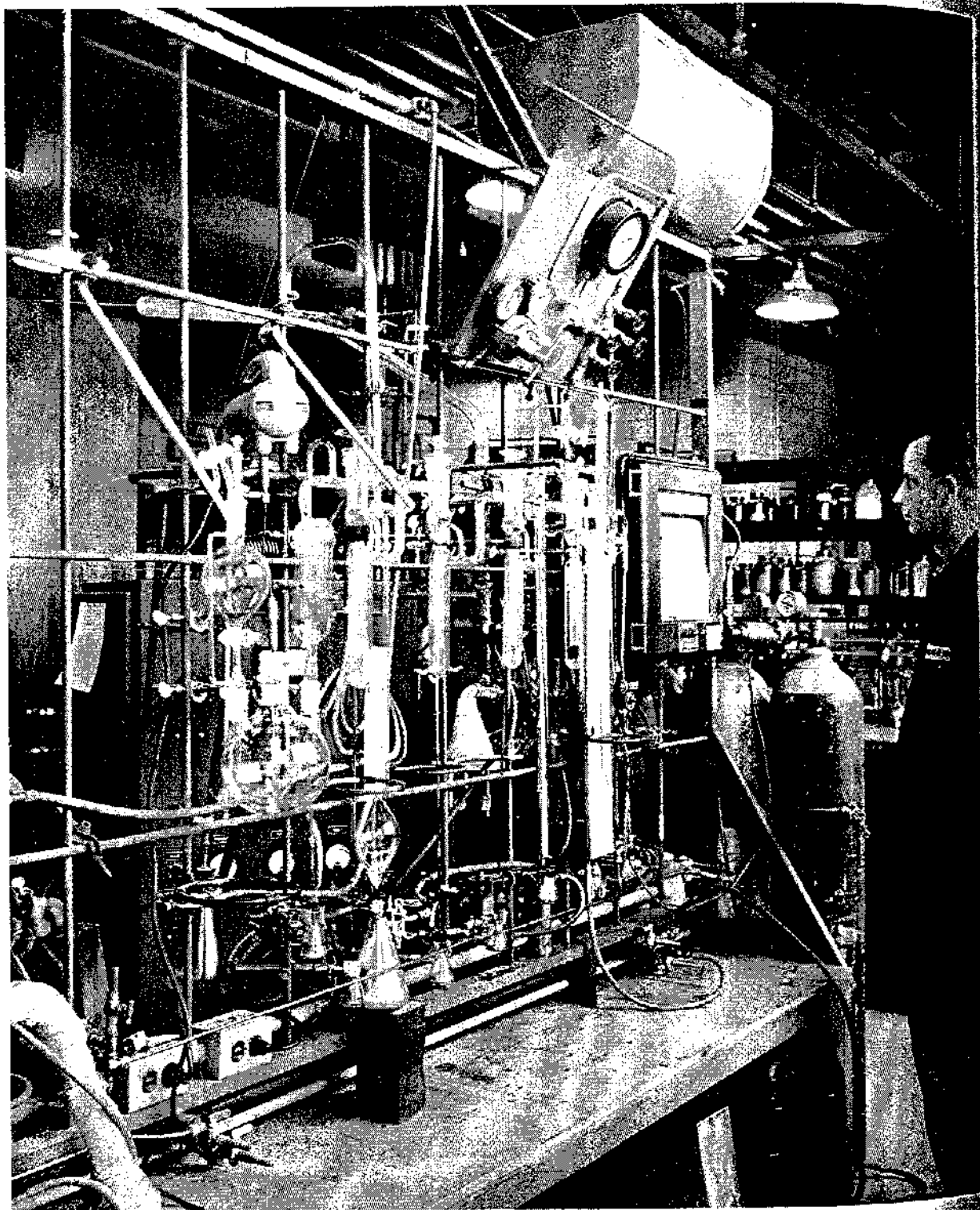


Figure 6. - Apparatus for boriding iron with diborane.



saturated with diborane vapor by passing it over the surface of liquid diborane maintained at a suitably low temperature.

Preliminary boriding experiments indicate that borides are not produced directly when reduced iron is treated with  $1B_2H_6 + 3He$  at  $150^\circ$  to  $250^\circ C$ . Under these conditions, elemental boron is apparently deposited on the surface of the catalyst. However, when such catalysts are heated overnight in helium at  $450^\circ$  to  $550^\circ C$ , partial conversion to iron boride may occur. The use of higher temperatures (for example  $600^\circ C$ .) does not appear to be desirable, because appreciable sintering of the catalyst may result. In several unsuccessful experiments nitrided iron was treated with diborane-helium mixtures to replace nitrogen atoms with boron. Enough data have not yet been obtained to justify any definite conclusions.

### Steel-Wool Catalyst

Commercial steel wool (grade 3) has been tested in the hydrocarbon synthesis. Like steel shot and lathe turnings, it was oxidized with steam (about 52 percent), alkalinized with potassium carbonate and reduced with hydrogen before synthesis. It had an exceptionally high activity, 211 at an average temperature of  $251^\circ C$ , as compared with 83 and  $264^\circ C$ . for 1018 steel, and yielded a product with relatively high average molecular weight. A test at high temperatures and space velocities, to obtain information as to its suitability for hot-gas recycle operations, was unsuccessful. Carbon deposition was rapid, probably because of inadequate heat transfer in the small fixed bed.

### Metal Hydrocarbons

The structure and behavior of metal hydrocarbons (compounds composed of iron, cobalt, or nickel, hydrogen and carbon monoxide) were studied because these compounds, like Fischer-Tropsch catalysts, can act as transfer agents for hydrogen and carbon monoxide. Investigation of cobalt hydrocarbonyl by spectroscopic and nuclear resonance methods led to the conclusion that the hydrogen atom probably is attached to the cobalt atom. This result requires revision of the current view that hydrogen is attached to oxygen and throws new light on the mechanism of formation and decomposition of hydrocarbons as well as their stability and reactions with various substrates. A study of hydrogen transfer by way of metal hydrocarbons may provide information concerning the mechanism of hydrogen transfer and chain lengthening in the Fischer-Tropsch reaction.

Previous work with cobalt carbonyls and hydrocarbons has provided information concerning the mechanism of addition of carbon atoms to unsaturated hydrocarbons and some indications as to the nature of adsorbed intermediates in the Fischer-Tropsch process. As iron has displaced cobalt in the Fischer-Tropsch process, investigations of iron hydrocarbonyl and substituted iron carbonyls are now in progress. The difference in chemical reactivity between cobalt and iron hydrocarbons may well provide a partial explanation for the different selectivities of cobalt and iron in the Fischer-Tropsch process.

Complexes similar to those previously prepared,

