

Figure 2. - Pilot plant for removing carbon dioxide from synthesis gas.

solution of potassium carbonate is used and greater steam economy achieved. In the 1952 Annual Report, measurements of the equilibrium partial pressures of carbon dioxide in hot solutions of potassium carbonate were described, and the results from a small pilot plant employing countercurrent scrubbing were given. Because the towers in this plant were considerably shorter than those used generally, a larger unit has been installed, comprising a 6-inch-diameter absorber of 30-foot packed height and an 8-inch-diameter regenerator with a 25-foot packed section (see fig. 2). The entire unit, except for a stainless steel pump and regenerator condenser, was constructed of mild carbon steel. Corrosion has been eliminated by adding 0.2 percent of potassium dichromate to the carbonate solution.

The data show that when a feed gas, saturated with water vapor, is used at 300 p.s.i.g. pressure and at the temperature of the carbonate solution, steam required for the removal of carbon dioxide can be reduced to about 40 percent of that used in the amine process, if the carbon dioxide content of the gas is reduced from 20 percent to 2. Costly heat-exchange equipment is eliminated, the quantity of cooling water is reduced, and loss of scrubbing agent by volatilization is eliminated.

Bench-Scale Experiments

Catalyst-Oil Slurry Process

Several experiments were made in the slurry reactors with different types of catalyst. Alan Wood magnetite was shown to be a very desirable catalyst in small, fixed-bed reactors. In activity and product distribution, the magnetite was similar to promoted, fused iron. Although the cost of catalyst is not a major factor in the price of synthetic liquid fuels, difficult preparations of catalyst should be avoided if possible. Preparation of this concentrated ore for the slurry process involved merely sizing and impregnation with alkali before the usual reduction and activation required in the slurry process.

In 31 days of continuous operation at 300 p.s.i.g., 300 hourly space velocity of $\text{H}_2 + 100$ synthesis gas, and 280°C ., 71.5 percent of the gas was converted. The product contained 24 percent $\text{C}_1 + \text{C}_2$ and 76 percent of C_3 and higher carbon-number compounds, almost all of which boiled in the gasoline range (below 204°C .). This test was repeated in a larger unit with some recycling of end gas. The catalyst was reduced more thoroughly (90 percent instead of 80), and the operating temperature was lower, 260° as compared with 280°C ., but the degree of conversion was the same. Furthermore, the yield of light hydrocarbons was decreased to 20 percent of the total hydrocarbons formed. The condensed hydrocarbons were again predominantly gasoline. An increase in the average temperature of 10°C . raised the conversion to 82 percent. The yield of gas increased only slightly. Failure of a fitting forced discontinuance of this test after 736 hours.

Improved distribution of product was obtained by operation in two stages. Two experiments were made in which 2 small reactors were operated in series. Between the two reactors, condensable hydrocarbons and water were removed from the effluent gases from the first unit, which were then passed through the second. In both cases the catalyst was impregnated magnetite ore. The first reactor contained 200 grams of iron per liter of slurry, the second only 100 grams per liter. Both catalysts were active, but the temperature in the second reactor had to be 14°C . higher to attain the same extent of conversion. The distribution of product was improved by this arrangement of reactors. The yield of $\text{C}_1 + \text{C}_2$ was only 13 percent of the total hydrocarbons, and the balance was largely gasoline. Only minor amounts of oxygenated compounds were produced on impregnated magnetite. As the usage of hydrogen and carbon monoxide was very close to that of the feed gas, the gas was used as efficiently in this series arrangement as in operation with recycling.

For some time Bentone-34 has been used as a suspension aid, to retard settling of catalyst. New techniques are now being studied for preparing gels and adding them to the reactors, and the causes for settling during reduction and synthesis are being investigated. For example, a synthetic ammonia catalyst, without a suspension aid, was reduced and activated by the best known procedures. When the activity decreased after about 500 hours, the slurry was cooled in place, withdrawn as a solid wax rod, sampled, and analyzed. About half the catalyst was in the lowest few inches of the bed; the remainder was evenly distributed through the reaction zone. Corresponding experiments with suspension aid have not yet been completed.

Hot-Gas-Recycle Process

One of the methods devised to remove the heat of the synthesis reactions employs a "dry", fixed bed of catalyst, over which is recirculated a sufficiently large amount of partly cooled exit gas to control the temperature. This "hot-gas-recycle" process can be operated at 300° C., a substantially higher temperature than is practicable for the oil circulation and slurry processes. At the higher temperature yields of gasoline are increased, and the yield of heavy hydrocarbons is decreased. A fluidized process, employing finely powdered catalyst, can be operated at and above 300° C., but in large-scale operations difficulty has been experienced in removing the heat of reaction.

Michael in Germany originally investigated a hot-gas-recycle system in which 100 volumes of tail gas had to be recirculated per volume of fresh gas to limit the temperature rise across the catalyst to 10° C. Because of the large quantity of gas and lack of voids in the catalyst, the pressure drop across the bed was high. The cost of recirculating gas increased substantially the price of a gallon of product. Use of a catalyst bed in which void space is high and reduction of the flow of recycle gas decrease the pressure drop. Since steel lathe turnings can be packed to give a void volume of 92 percent, this material appears to have potential use in hot-gas-recycle operation.

To determine the energy costs for recirculation, measurements of pressure drop across a bed of lathe turnings were made and compared with those obtained with granular, 6- to 20-mesh fused iron. The recycle ratio of end gas to fresh gas was 28. The end gas had a density equivalent to that of an exit gas saturated with light hydrocarbon vapor. The energy costs of gas recirculation have been plotted as a function of the height of the catalyst bed (see fig. 3). For equal gas conversion, recycling cost of 0.5 cent per gallon of product was obtained for a 10-foot bed of lathe turnings, whereas with a bed of granular catalyst of the same height the cost was 20 cents. Use of the hot-gas recycle system with lathe turnings is being considered.

Catalyst-Testing Studies

Work is being done on developing catalysts that retain high activity for relatively long periods and produce a maximum yield of C₃+ hydrocarbons and minimum quantities of methane and ethane. Current investigations are being concentrated on three forms of iron - fused oxide, activated steel shot, and steel turnings. These materials are being tested at 300 p.s.i.g. and an hourly space velocity of 300 with 1H₂ + 1CO synthesis gas. As synthetic ammonia catalyst D3001 (Fe:MgO:K₂O:Cr₂O₃:SiO₂ = 100:6.92:0.91:1.12:0.94) is quite active and reproducible, it has been used as a standard for evaluating the performance of other catalysts.

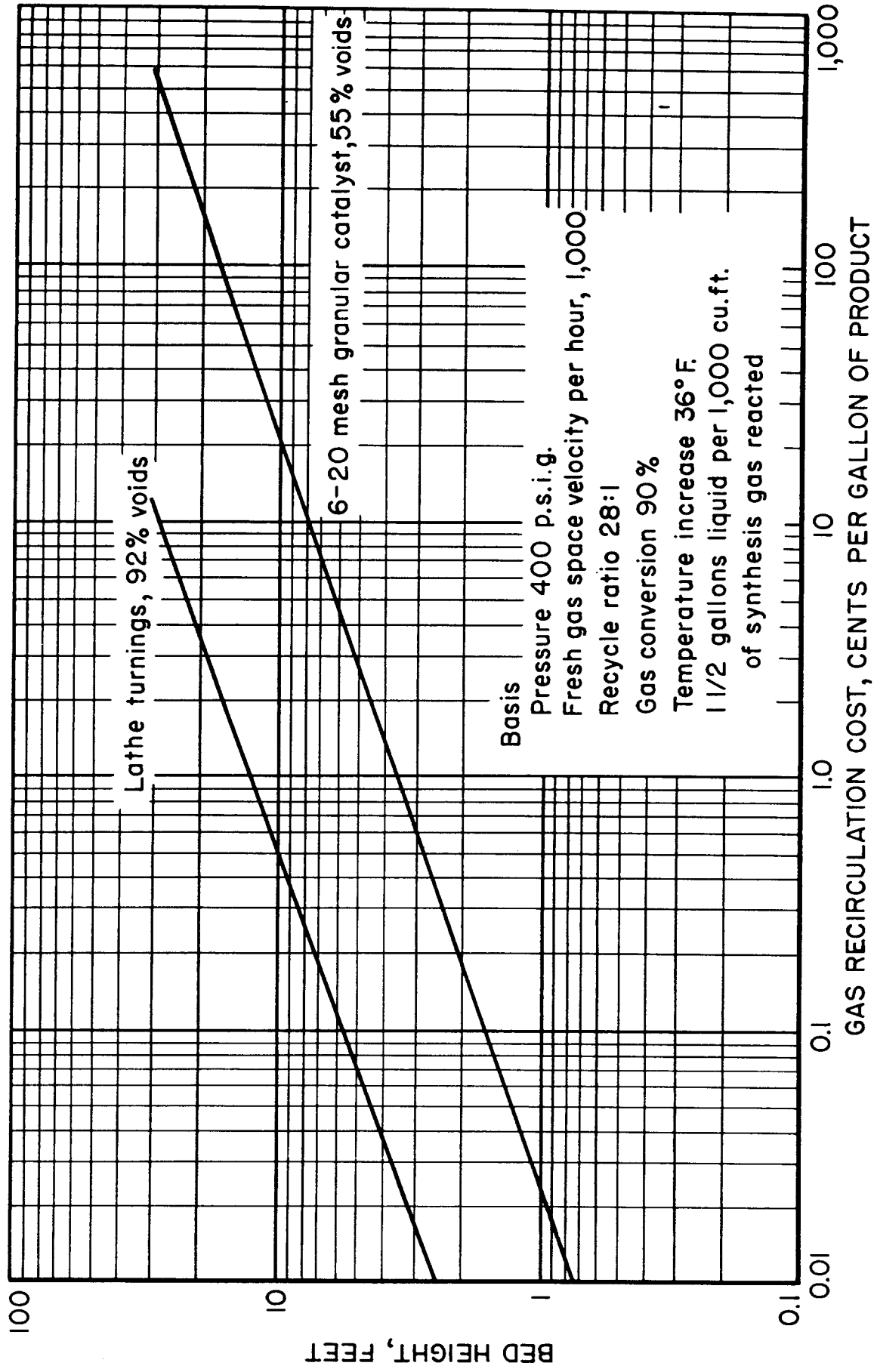


Figure 3. - Cost of gas recirculation.

Fused Iron

Two structural promoters (beryllia and thoria), in addition to those mentioned in the 1952 Annual Report, have been tested in both reduced and nitrided iron catalysts. Reevaluation of the data obtained with structural promoters showed that the type of oxide (MO , M_2O_3 , etc.) does not correlate with activity of the catalyst. Only ceria, silica, and zirconia appear to have marked beneficial effect on the activity of the reduced catalyst; boron oxide appeared to decrease the activity. Of the nitrided catalysts, only those containing titania and zirconia showed better activity than the unpromoted catalyst.

After the effect on activity of each structural promoter had been determined, five were selected for a series of tests to determine the concentrations of promoter necessary for maximum activity and optimum selectivity. Magnesia, alumina, silica, calcium oxide, and manganese oxide were tested at various concentrations in both reduced and nitrided iron. Of the reduced catalysts, preparations containing 1 to 4 parts of structural promoter per 100 parts of iron (depending on the promoter selected) were the most active. No significant change was noted in product distribution as a result of a change in promoter concentration. Except for alumina, structural promoters did not improve the activity of nitrided iron in the range of concentrations tested. One part of alumina per 100 parts of iron increased the activity about 30 percent over that of the unpromoted catalyst.

In a study of the effect of alkali, fused iron containing 0.5 and 1.0 to 1.5 mole-percent of lithium, sodium, potassium, and rubidium oxides is being tested in both the reduced and nitrided states. Preliminary results indicated that the activity increased with the atomic number of the alkali. With the lower concentration of alkali, reduced iron containing rubidium oxide was approximately 10 times as active as unpromoted iron. Furthermore, this catalyst when nitrided produced about 20 percent more gasoline than the nitrided, unpromoted catalyst. At the higher concentration of alkali, rubidium oxide was still the most active promoter for both the reduced and nitrided catalysts. The reduced catalyst produced one-third less methane than the unpromoted sample, while the nitrided one produced about 16 percent more gasoline than the unpromoted sample.

Impregnation of fused iron with 0.01 percent copper (from a 1-percent solution of copper oxide) before reduction increased the activity of the reduced preparation by 50 percent and that of the nitrided preparation by 20 percent, compared with those of the respective unimpregnated preparations. Product distributions in each case were not significantly affected.

Massive Iron

Steel Spheres

Optimum reduction conditions for 1/16-inch oxidized-steel shot appear to be 400° C. with 1,000 hourly space velocity of hydrogen for 8 hours. This treatment produced the highest activity coefficient and maximum gasoline yield, about 53 percent of the total hydrocarbon product. Promoter studies showed that about 0.02 percent of alkali (as K_2O) on steel spheres gave maximum activity and gasoline yield. This amount of alkali also resulted in slightly lower methane production than other concentrations.

Carburization with $1H_2 + 1CO$ and subsequent oxidation, addition of alkali, and reduction was investigated as a method of pretreating 1/16-inch steel spheres. Within the range of carburization temperatures studied, 325°-500° C., the sample

treated at 450° C. had the highest activity. Selectivity data for the carburized-steel spheres show a decrease in C₁ to C₄ hydrocarbon production up to a carburization temperature of 375° C. and a corresponding increase in yields of liquids and solids. Carburization above this temperature did not change the product distribution further. However, the largest amounts of C₂, C₃, and C₄ unsaturates were produced by catalysts carburized above 375° C.

Lathe Turnings

In a series of tests on catalysts composed of lathe turnings from three types of cold-rolled carbon steels (SAE 1018, 1042, 1095), the highest activity was obtained from the steels having the lowest carbon content (1018, 1042). The largest yields of products in the gasoline range (52 percent of the total hydrocarbon product) were obtained from the 1018 turnings.

The most effective pretreatment was double oxidation with steam at 600° C., followed by reduction of the oxide in each case and impregnation with a solution of 2-percent potassium carbonate after the second oxidation. This amount of potassium carbonate increased the activity 30 percent compared with that of a catalyst to which no alkali had been added. Furthermore, addition of alkali resulted in increased average molecular weight of hydrocarbons, increased yield of gasoline, and decreased production of methane.

The optimum concentration of potassium oxide appeared to be 0.06 percent, considerably lower than for fused catalysts (about 0.35 percent). These turnings were impregnated with a solution of 5-percent potassium carbonate. Selectivity data show that an increase in the alkali concentration up to 0.15 percent caused a progressive decrease in C₁ to C₄ production and an increase in the yield of liquids and solids. The amount of unsaturates in the C₂ fraction also increased with the alkali content. Infrared analyses showed that the yield of alcohol in the product fractions boiling up to 352° C. was greatest with the highest alkali concentration (0.15 percent potassium oxide).

A life test of 23 weeks has been completed on 1018 carbon steel turnings. This catalyst was very stable and more active than some fused iron catalysts.

Catalyst Characterization, Kinetics, and Reaction Mechanism

Catalyst Studies

A method was developed for determining surface areas of massive iron catalysts. This method involves the use of argon as the adsorbate instead of the more commonly used nitrogen. Massive iron catalysts that have been oxidized and reduced have surface areas of only about 0.8 square meter per gram. Although surface areas of fused catalysts were considerably higher, 5 to 10 square meters per gram, the activities of both types of catalyst were about the same. These data confirm the earlier postulate that the active zone of the catalyst is confined to a layer extending only a short depth from the external surface.

To supplement the information obtained from activity tests, a study was made of surface areas as well as rates of carburizing and nitriding of fused iron containing a variety of promoters. Pretreatment of a fused catalyst with methylamine at 250° C. showed that an iron carbonitride containing a ratio of 1 nitrogen to 3 carbon atoms can be prepared in 1 step.

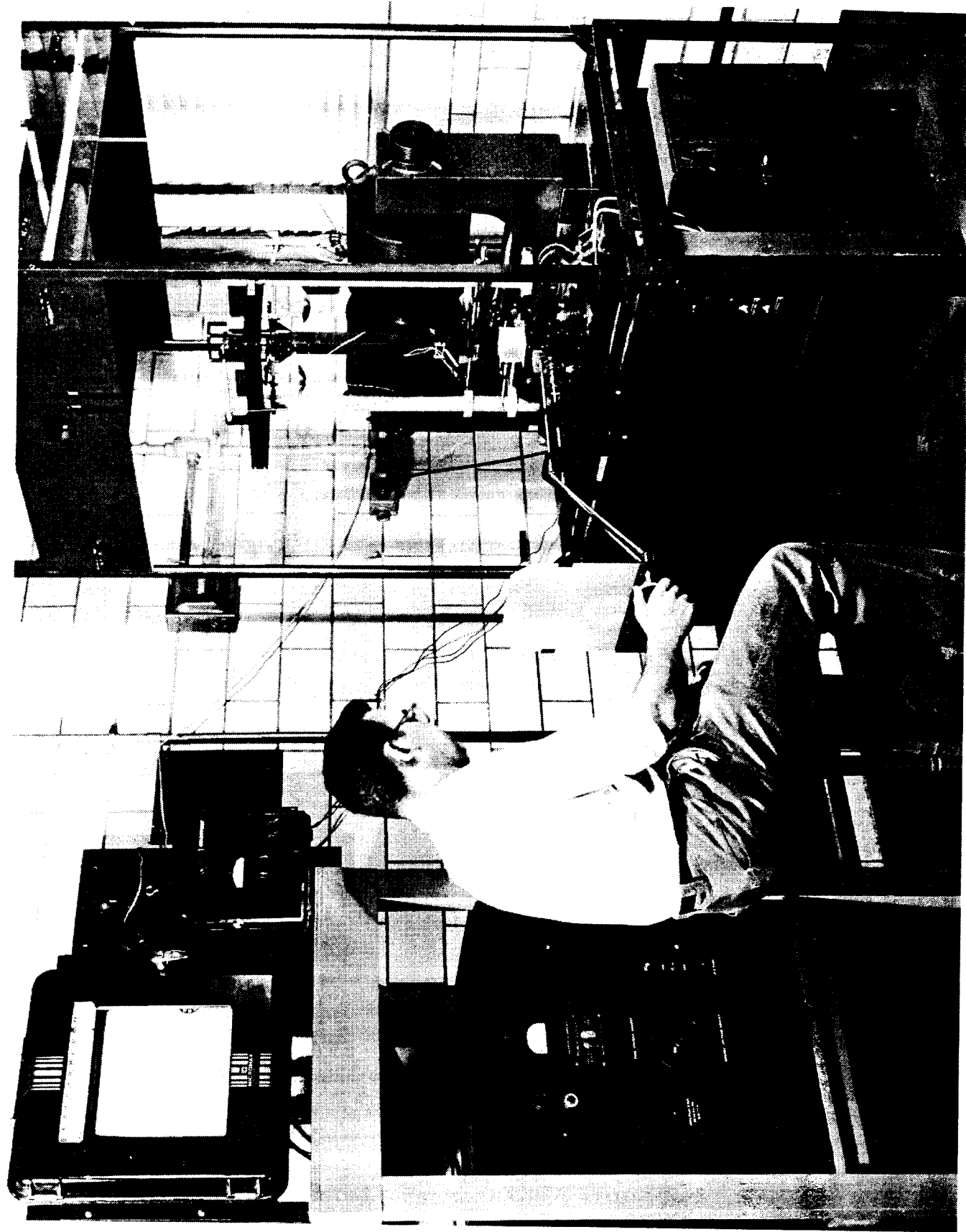


Figure 4. - Magnetic balance for thermomagnetic and kinetic studies of catalysts.

Pore-volume and surface-area studies of used fused iron, either reduced or reduced and nitrided initially, showed that the presence of nitride increased the stability of the structure and its resistance to oxidation during synthesis. The reduced catalyst had been expanded during synthesis, perhaps due to carburization, but the nitrided catalyst had contracted, even though carbon had replaced nitrogen.

Behavior of Carbides

One of the undesirable side reactions of the Fischer-Tropsch synthesis is deposition of carbon in the catalyst. To ascertain whether thermal reactions of iron carbides might cause this deposition and to learn more about the nature of iron carbides, the transition from hexagonal close-packed (h.c.p.) iron carbide to Hägg iron carbide and the reaction of higher iron carbide with metallic iron to form cementite were studied in a copper- and alkali-promoted iron catalyst by means of a magnetic balance (see fig. 4).

The transition from h.c.p. to Hägg iron carbide was heterogeneous, with no apparent change of the compositions of both carbides, or any detectable solubility of one carbide in the other. The data confirmed the narrow range of composition of Hägg carbide and the fact that it contains somewhat more iron than corresponds to the formula Fe_2C .

The synthesis of cementite from metallic iron and higher iron carbide proceeded via Hägg carbide and only above about $320^{\circ}C$. It did not go to completion up to $440^{\circ}C$.; above that temperature, decomposition of Hägg carbide into cementite and free carbon was rapid enough to prevent completion of the synthesis.

The data show that deposition of carbon on iron catalysts during the Fischer-Tropsch synthesis is not caused by thermal reactions of iron carbides, unless h.c.p. iron carbide should contain more carbon than Hägg iron carbide.

Kinetics of the Synthesis

Data have been obtained on the kinetics of hydrogenation of carbon monoxide on nitrided iron catalysts. The general method involved tests in which the conversion was varied by changing the rate of flow of synthesis gas over a constant volume of nitrided iron at constant temperature. Fused iron (catalyst D3001) was used in a tubular, fixed-bed reactor. Data on the consumption of synthesis gas and formation of gaseous products were obtained from measurement and analysis of the feed and exit gases. Synthesis gas varying in composition from $2H_2 + 1CO$ to $0.25H_2 + 1CO$ was used at 225° and $240^{\circ}C$. and 300 p.s.i.g. The effect of pressure in the range 50 to 300 p.s.i.g. was studied, with $1H_2 + 1CO$ at $240^{\circ}C$.

The data approximately fit the equation $-\ln(1-x) = k/S$ up to about $x = 0.7$ for a variety of feed gas ratios and at both temperatures, where x is the fraction of $H_2 + CO$ consumed, k the rate constant, and S the space velocity. The activation energies averaged 20 kilocalories per mole and showed a remarkable constancy over a wide range of feed gas ratios. The average activation energy obtained by comparing space-time yields (xS) at the same conversion was 19.1 kilocalories.

The data obtained at different pressures fit the equation $-\ln(1-x) = k''P/S$ very well; that is, the rate was proportional to the pressure, P .

From the same studies, data were obtained on the selectivity of the Fischer-Tropsch synthesis on nitrided-iron catalysts. As synthesis gas was converted more completely, the consumption of hydrogen decreased, passed through a minimum, and then increased. The formation of methane, relative to synthesis gas consumed, followed a

similar curve. The olefin content of the C₂ and C₃ fractions decreased with conversion. The selectivities varied rapidly with changes in the hydrogen - carbon monoxide ratio in the feed gas. Relative usage of hydrogen and formation of methane increased with hydrogen content of the feed gas, whereas unsaturation in the C₂ and C₃ hydrocarbons decreased.

Reactions of Synthesis Gas in Presence of Metal Carbonyls

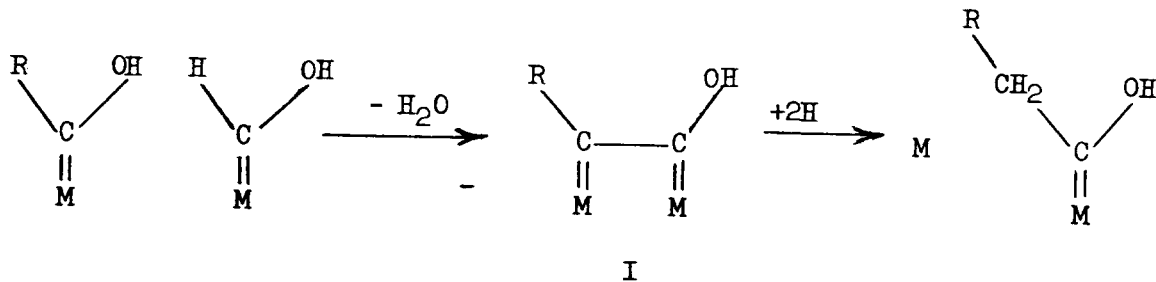
It has been postulated that incipient carbonyls are formed on the surface of a Fischer-Tropsch catalyst and that chain lengthening occurs on the catalyst surface by the addition of one carbon atom at a time to the end of a growing chain. The manner in which this chain growth is brought about is not known, although a mechanism has been proposed for the Fischer-Tropsch reaction that is based on sound principles. A study of the chemistry of metal carbonyls has led to the discovery that the chain length of an unsaturated hydrocarbon can be increased by 1 carbon atom by reaction of the hydrocarbon with pure cobalt hydrocarbonyl, HCo(CO)₄, in a homogeneous system. The reaction between cobalt hydrocarbonyl and the substrate proceeds smoothly at or below room temperature and is complete within a few seconds. Table 1 shows the products obtained from various substrates and illustrates the variety of reactions possible in the presence of cobalt hydrocarbonyl.

TABLE 1. - Products from various substrates by reaction with cobalt hydrocarbonyl

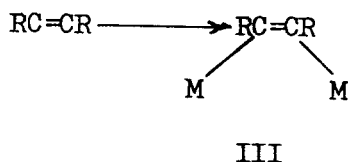
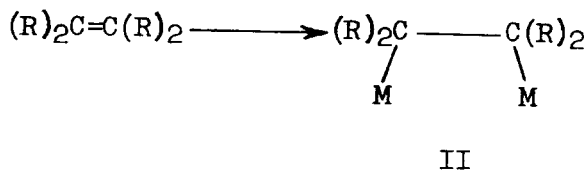
Substrate	Products	Type of reaction
Cyclohexene	Cyclohexanecarboxaldehyde	Hydroformylation
Hexene-1 (excess)	C ₇ aldehydes	do.
	Hexene-2	Isomerization
	Hexene-3	do.
-Methylstyrene	Isopropylbenzene	Hydrogenation
	C ₁₀ aldehydes	Hydroformylation
Benzyl alcohol	Toluene	Hydrogenolysis
Benzhydrol	Diphenylmethane	do.
Triphenyl carbinol	Triphenylmethane	do.

Although the presence of a hydrocarbonyl as an intermediate in the Fischer-Tropsch synthesis has not been established, complexes composed of a transition metal, carbon monoxide, and hydrogen may well be formed on the surface of the catalyst. The reaction of cobalt hydrocarbonyl with various substrates described above is significant in that it provides the first proof that a compound composed of a transition metal, carbon monoxide, and hydrogen can act as a transfer agent for hydrogen and carbon monoxide. The electron transfers are easier to follow in this homogeneous system, and a study of the mechanism of the reaction between cobalt hydrocarbonyl and organic compounds may prove fruitful in helping to elucidate the mechanism of the Fischer-Tropsch reaction.

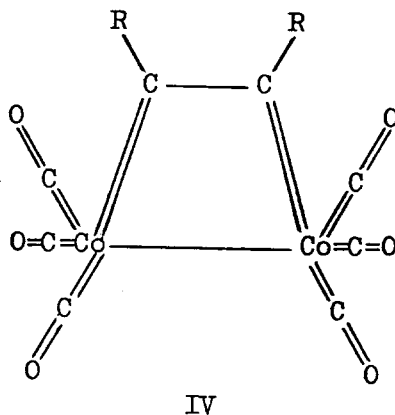
Another study has furnished a clue to the manner in which the growing chain is attached to the catalyst surface. Chain growth in the Fischer-Tropsch reaction has been explained by the following mechanism:



Hydrogenation of acetylenes and olefins as well as the metal-catalyzed isomerization of double-bonds in olefins are thought to involve the following intermediates:



The structure common to these intermediates (I, II, III) involves an M-C-C-M linkage. However, organometallic complexes of transition elements possessing this type of linkage have not been known. Now, stable compounds containing this M-C-C-M linkage may be readily prepared by treating dicobalt octacarbonyl with substituted acetylenes to give IV, a compound similar to the postulated Fischer-Tropsch intermediate (I).



Compounds having a structure such as IV will probably be useful for studying the mechanism of the Fischer-Tropsch and other heterogeneously catalyzed reactions.

The assignment of structure IV to the hexacarbonyl is based on evidence from infrared spectra. The surprising stability of these complexes can be explained by a detailed analysis of types of chemical bonds present. The possible role of these compounds in the Fischer-Tropsch and related processes is under investigation.

Separation and Identification of Fischer-Tropsch Products

The products of the Fischer-Tropsch and coal-hydrogenation processes are complex mixtures. The first, and frequently only, step in separating such mixtures is fractional distillation. In certain cases, however, complete separation by fractional distillation is impossible or impractical. A concentrate prepared by efficient fractional distillation often can be further separated into fractions of different molecular type by extractive or azeotropic distillation.

Separation of mixtures by any type of distillation depends upon differences in the volatilities of the materials to be separated. To modify these volatilities, certain solvents may be added before extractive or azeotropic distillation.

In azeotropic distillation a volatile component which forms a constant boiling mixture with one or more components of the original mixture is added. Usually the solvent is added with the charge, and conventional stills may be used without further modification. Vapor-liquid extraction, or extractive distillation, on the other hand, involves distillation in the presence of a substance that is relatively nonvolatile compared with the components to be separated. In this case, the component is added continuously near the top of the distilling column so that an appreciable concentration is maintained in the liquid phase throughout the column. In the proportions used, the solvent is miscible with the mixture to be separated at the temperature of the distillation. Ordinary equipment for fractional distillation must be modified to allow continuous introduction of solvent and prevent accumulation of large quantities of solvent in the still pot.

A batch unit suitable for recycling of solvent was designed and constructed (see figs. 5 and 6). Except for the stillpots, which were especially designed, the glass parts were made from vacuum jacketed and silvered columns. The operability of this apparatus depends on maintaining constant the solvent and reflux rates in each column. Extractive distillations do not yet appear to have been carried out under vacuum. This apparatus was designed for use at reduced as well as atmospheric pressures. It was tested at 35-mm. Hg pressure with a high-boiling solvent, triethyleneglycol. Results showed that extractive distillation may be of great value for separating complex organic mixtures or isomeric substances.

With cobalt-thoria catalysts the Fischer-Tropsch process produces only about 1 percent of oxygenated products. With iron catalysts, the process yields a product in which as much as 18 percent of the converted carbon monoxide may appear as oxygenated organic compounds, distributed about equally between the oil and water streams. The influence of changes in process variables or the effects of modified or new catalysts on the synthesis may be determined by following the changes in the reaction products. For this purpose, a scheme has been developed for separating and identifying the oxygenated compounds in Fischer-Tropsch oils. Acids were isolated by extraction with alkali, and alcohols were removed from the oil by phthalation and subsequent hydrolysis of the phthalate ester. Esters of low molecular weight could be removed by saponification, but some difficulty was experienced with esters of high molecular weight; these do not saponify readily. Ketones were converted to the corresponding secondary alcohols and removed as such from the oil. Considerably more work is required to develop a method for isolating aldehydes quantitatively. However, the experience obtained and the techniques evolved in this work have given a firm foundation for handling the various oxygenated mixtures produced in the Fischer-Tropsch process.

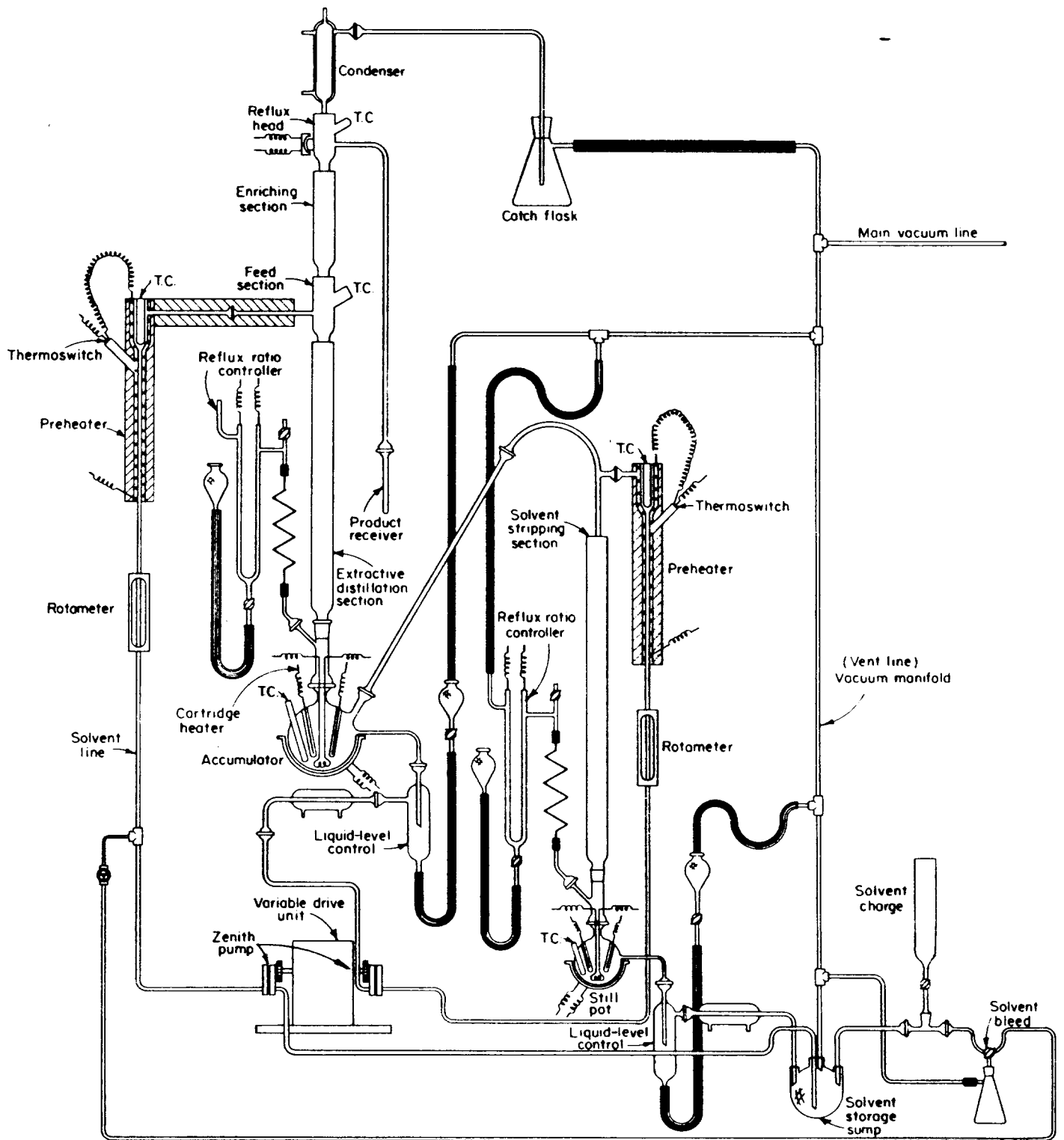


Figure 5. - Schematic diagram of batch extractive distillation column with solvent recycle.

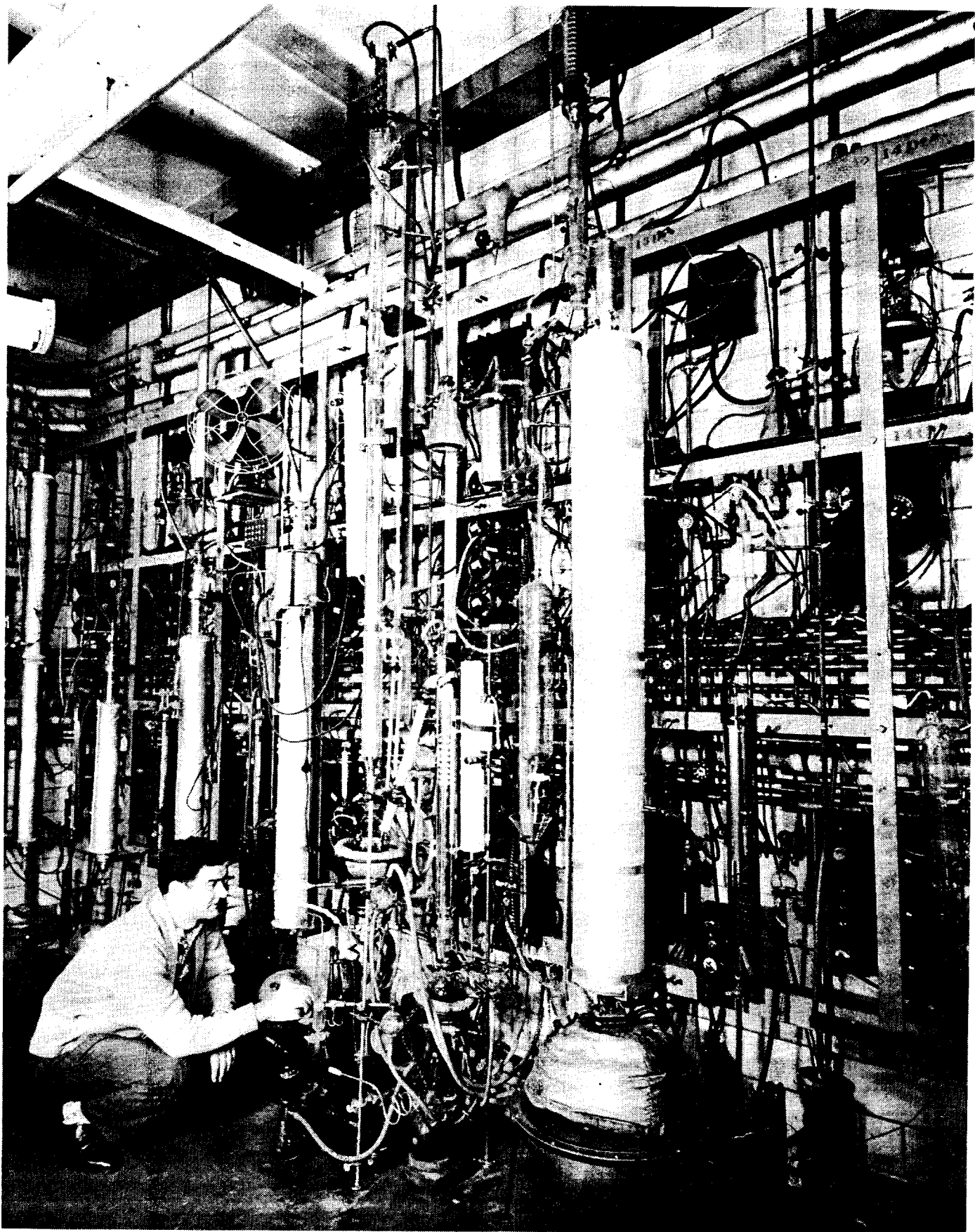


Figure 6. - Batch extractive distillation column with solvent recycle.

In addition, a method has been developed for determining the structure of higher alcohols found in Fischer-Tropsch oils. The alcoholic components of a sample are isolated by phthalation, and the alcohols are then recovered by saponification. After fractional distillation, the alcohols are identified by conversion to paraffin hydrocarbons of the same structure and also by conversion to the next lower paraffin from which the carbon that bears the functional group has been removed. Alcohols up to C₉ have thus been identified. The structure of acids also can be determined by first reducing them to alcohols and then, using the procedure outlined above, determining the structure of the alcohol.

Spectrometric Analysis of Alcohol Mixtures

A method has been developed for spectral analysis of higher alcohols, principally for application to alcohols obtained from Fischer-Tropsch syntheses. Mass spectra of 37 alcohols, ranging from methanol to undecanol, have been obtained and their fragmentation patterns compared. This study deals principally with alcohols C₁ to C₈. C₁₀ and C₁₁ normal alcohols have been studied only qualitatively. Alcohols are considered to be of three major types: Primary, secondary, and tertiary. For this study, the primary group has been divided into two classes: (1) Normal (straight-chain), and alpha-branched and (2) beta-branched. Secondary alcohols may be classified as 2-, 3-, 4-, etc., types. Major peaks have been related to the structures of the compounds. The following general rules hold for the alcohols investigated:

1. For primary straight-chain, primary branched, and naphthenic alcohols, the first and second major peaks below the parent peaks result from loss of water followed by loss of a hydrocarbon group. The spectra are similar to the spectra of the corresponding olefins.

2. For secondary straight-chain, secondary branched, and tertiary alcohols, the first and second major peaks below the parent peaks result from loss of a hydrocarbon group followed by loss of water. The base peak always results from the loss of hydrocarbon groups due to splitting at the carbinol group. These data may be applied to determine quantitatively the various types of alcohols in a complex mixture or specific alcohols in less complex multicomponent mixtures.

In a cooperative project with the Explosives Branch of the Bureau of Mines, the mass spectrometer was applied to analyses of oxides of nitrogen. Conventional methods for analyzing mixtures containing nitrogen dioxide (nitrogen tetroxide) are difficult and time consuming, and the erratic behavior of nitrogen dioxide in the mass spectrometer has prevented accurate spectrometric analysis thus far. After elimination of instrumental instability, a method was developed for analyzing mixtures of nitrogen dioxide, nitric oxide, nitrous oxide, carbon monoxide, carbon dioxide, nitrogen, oxygen, hydrogen, and water vapor. Determination of all components except nitrogen dioxide was accomplished readily by routine methods. Analysis for this compound required preconditioning of the apparatus. For partial pressures of nitrogen dioxide 15 to 200 microns behind the mass-spectrometer leak, the sensitivities for the principal mass peaks were reproducible and almost independent of partial pressure. Day-to-day reproducibility of these sensitivities was comparable with that for hydrocarbon gases. Below 15 microns, the nitrogen dioxide spectrum changed rapidly, with decreasing partial pressure; but the reproducibility of spectra on a particular day and at a given pressure made possible the analysis of nitrogen dioxide, even in this range of partial pressures. Conditioning, calibrating for nitrogen dioxide, and analysis of 20 mixtures required an 8-hour shift. Nevertheless, this analysis is much more rapid than older chemical methods. The accuracy of the analysis depends upon the concentration of nitrogen dioxide. The ultimate limit of detectability is about 0.05 mol-percent.

Sulfur Analysis of Synthesis Gas

An accurate, rapid control method is being evolved for analysis of total sulfur in Fischer-Tropsch gas. The method consists of passing the gas over a heated, platinum spiral to convert organic sulfur to hydrogen sulfide which is determined by the methylene-blue method. Conversion of sulfur in gaseous, sulfur-containing compounds to hydrogen sulfide must be quantitative. Suitable all-glass apparatus was developed, and initial calibration tests were made. Thiophene was the first compound studied because it is most resistant to conversion. Approximately 30 runs showed that conversion of sulfur in thiophene to hydrogen sulfide is complete at spiral temperatures of 870° to 1,000° C. With closer control of flow or at flow rates less than the normal rate of 0.5 cubic foot of gas per hour, conversion probably can be complete at temperatures as low as 800° C.

Further tests will be made with ethyl mercaptan if it can be purified sufficiently. Work is currently being done on purification of a technical grade by a method involving freezing and recrystallization. Distillation methods were unsuccessful.

Synthesis of Liquid Fuels by Hydrogenation of Coal

Process Development

High-Temperature Hydrogenation

Batch autoclave experiments at high temperatures were described in the 1952 Annual Report. At temperatures above 500° C. and hydrogen pressures of 7,000 to 8,000 p.s.i.g., coal, in the presence of active catalysts and with or without vehicle oil, could be converted rapidly to a distillable oil containing a high percentage of gasoline. These results indicated the possibility of replacing the two or more steps in the conventional coal-hydrogenation process by a single step. If the production of a continuous plant can be limited to distillable oils, and if these can be used as a vehicle for further processing, removal of solids and recovery of catalyst would be greatly simplified. Furthermore, the oil losses heretofore incurred in removal of solids would be greatly decreased.

To investigate the process in a continuous unit, tests were made in which a coiled tube was used as reactor. The feed stock consisted of finely powdered Rock Springs, Wyo., coal suspended in oil (40 parts of coal and 60 parts of oil by weight). The coal was neutralized with sulfuric acid and impregnated with ammonium molybdate equivalent to 1 percent molybdenum. The vehicle oil was the 200° to 325° C. fraction from a middle oil produced at the Synthetic Fuels Demonstration Plant at Louisiana, Mo. In a single-pass run made at 538° C., 8,800 p.s.i.g., a feed rate for coal paste of 120 gm. per hour, and a flow of hydrogen of about 17 cubic feet per hour, 82 weight-percent of the feed (vehicle + coal) was converted to oil, and 30 percent of this oil was gasoline. The remaining oil had a higher boiling range than the vehicle oil. Operating conditions would have to be adjusted to reproduce the vehicle oil.

Future work will proceed simultaneously along two lines. First, work will be conducted in the small continuous unit (about 100 cc. of feed per hour) (see fig. 7) to obtain data on the hydrogen - coal ratio and the rate of throughput of coal. The second phase will be concerned with the design of the vessel. A basic run will be made in a cylindrical vessel, followed by a run in a packed vessel to obtain approximately the same high ratio of surface area to volume which prevails in the present coiled-tube reactor.

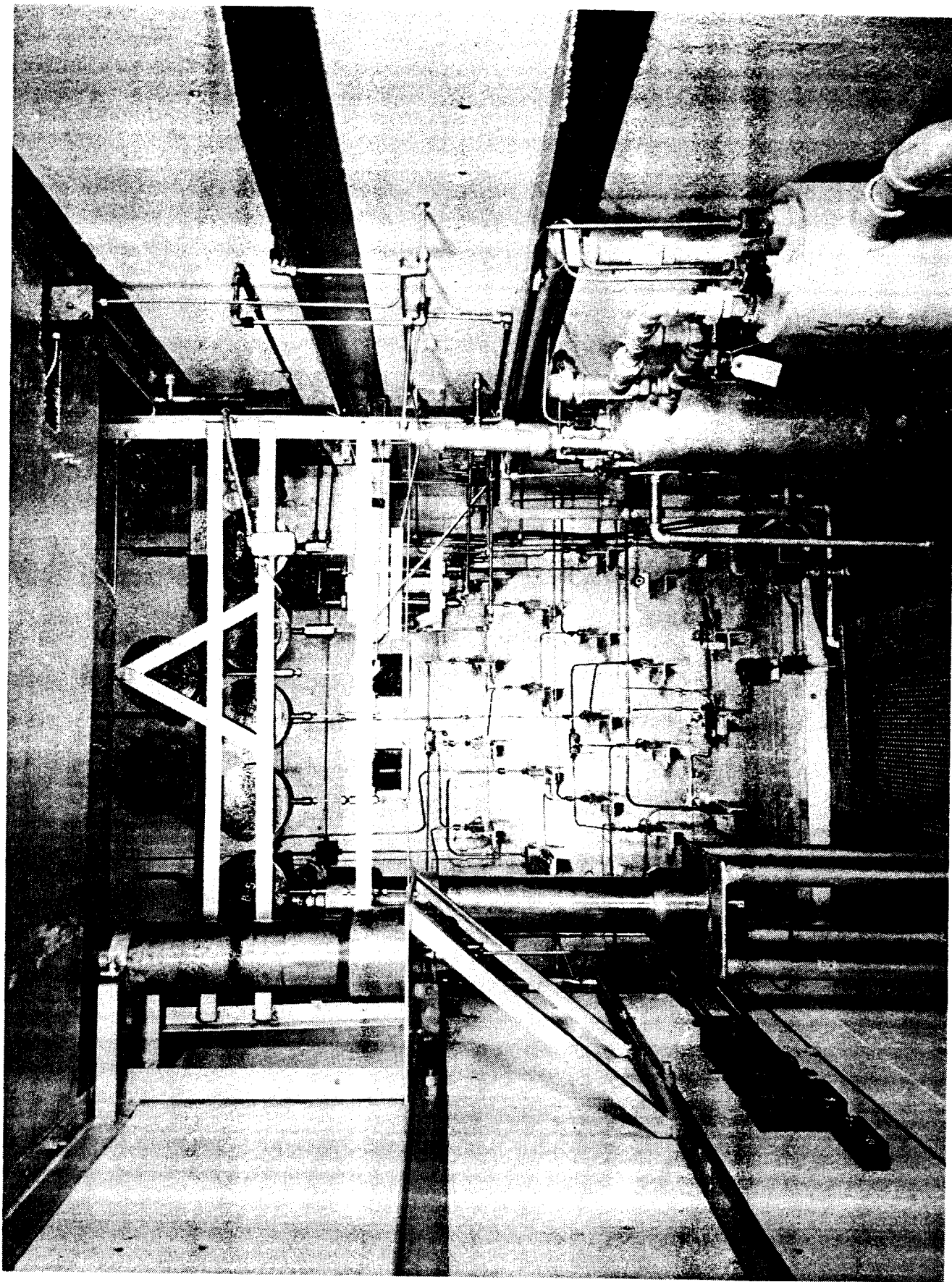


Figure 7. - Bench-scale continuous unit for studying high-temperature coal hydrogenation.

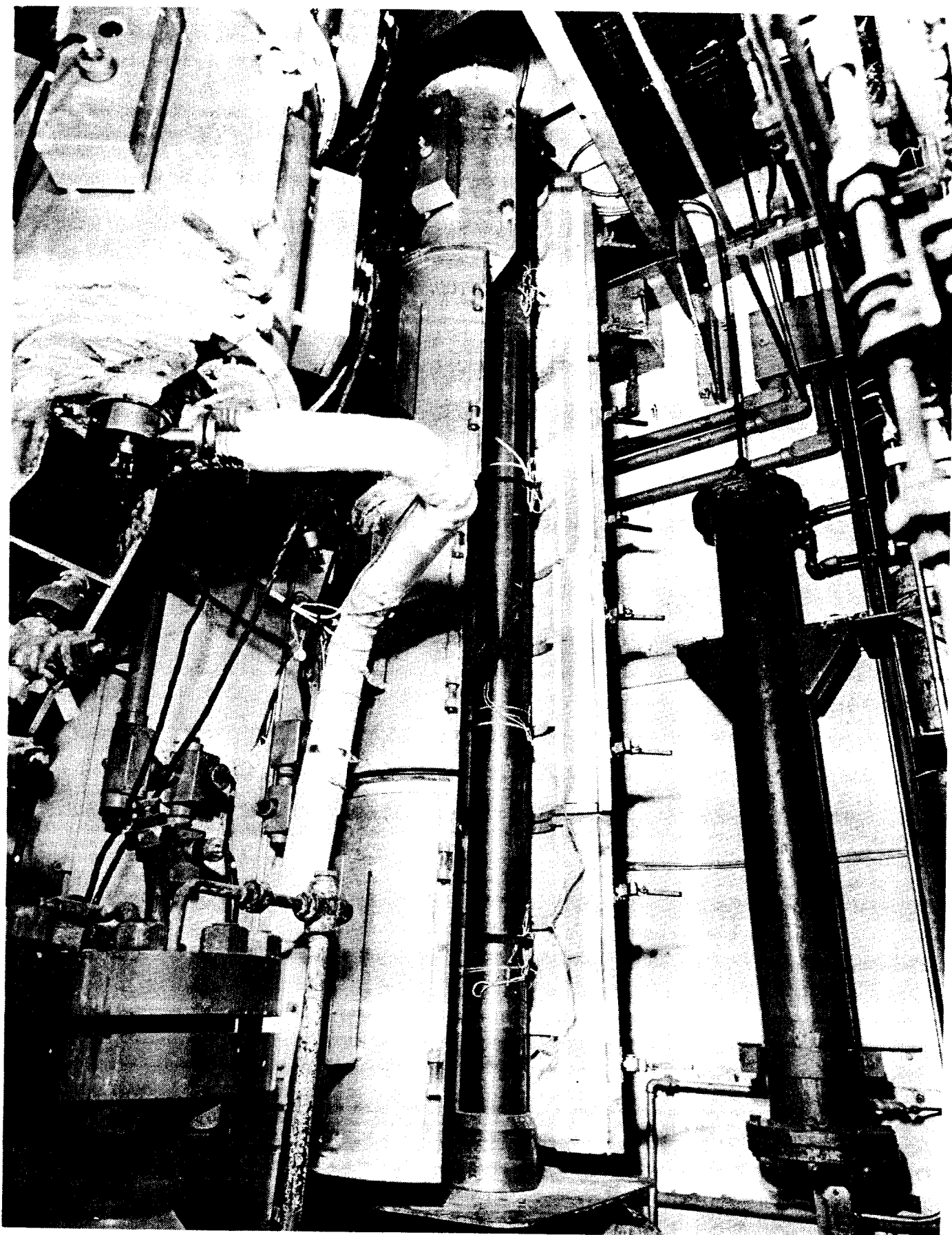


Figure 8. - High-temperature coal-hydrogenation pilot plant, showing reactor.

For these design studies, the liquid-phase pilot plant, which operated at 3,500 p.s.i.g., has been completely modified for operation at 10,000 p.s.i.g. (see fig. 8). This modification included installing new converters, changing compressor packing, installing automatic let-down valves, changing all safety valves and gages, developing a back-pressure regulator, changing all connecting lines, and extensive revisions in the low-pressure system. Development work to obtain longer compressor packing life included chrome plating of the piston, closer tolerances of piston guides, better combinations of packing, and improved lubrication of the packing. A continuous still has been designed, erected, and tested in several shift operations. The capacity of this pilot plant is about 30 pounds of feed per hour, but the first orientation experiments will be made with a feed rate of 8 pounds per hour.

Catalysts for Hydrogenation of Coal

Batch-autoclave tests have been made to (1) compare impregnation of ferrous sulfate on coal before hydrogenation with intimate mixing of coal and catalyst in a ball mill, (2) investigate the effect of neutralizing coal on hydrogenation, (3) study the kinetics of hydrogenation of lignite at 400° C., and (4) study nickelous sulfate as a catalyst for hydrogenation.

In tests of Kentucky coal obtained from the demonstration plant at Louisiana, Mo., two methods of applying ferrous sulfate were employed: (1) Intimate mixing of the dry ingredients in a ball mill and (2) impregnation of the coal by immersion in an aqueous solution of ferrous sulfate followed by drying. Both methods were effective, but impregnation resulted in lower yields of asphaltene, that is, material soluble in benzene but insoluble in n-hexane. These tests were conducted at 450° C., with an initial hydrogen pressure of 4,000 p.s.i. Time at reaction temperature was 1 hour.

Previous experience had indicated that neutralization of the basic ash of the coal with sulfuric acid increased the effectiveness of some of the catalysts. This effect was investigated for a number of catalysts in tests conducted at 4,000 p.s.i.g. initial hydrogen pressure, 450° C., and 1 hour at reaction temperature. The catalysts were applied by impregnation. Before catalyst was added, the coal (Rock Springs, D. O. Clarke mine, Superior, Wyo.) was 90-percent neutralized with sulfuric acid. Neutralization had little effect with 1 percent of molybdenum or tin. With 0.1 percent tin, neutralization reduced the amount of benzene-insoluble product. When ferrous sulfate, ferrous chloride, or cupric chloride was used, neutralization resulted in less asphaltenic products. In the case of cupric chloride, production of asphaltene was particularly low. Heretofore, such complete conversion at this temperature had been accomplished only in the presence of tin or molybdenum. The two chlorides had not shown pronounced catalytic effects in runs with unneutralized coal.

In runs without added catalyst, neutralization resulted in drastic reduction in benzene-insoluble material and doubling of the oil production. The effect of adding sulfuric acid may have been due to the sulfate ion or to the presence of sulfur rather than to neutralization itself. This point will be investigated further.

Lignite from the Velva mine, Ward County, N. Dak., was hydrogenated for periods ranging from 17 to 185 minutes at 400° C. and initial pressures of 1,000 to 4,000 p.s.i.g. The main product at this temperature was asphaltene, as with subbituminous coal. Conversion of benzene-insoluble matter followed a first-order rate law, and the specific reaction-rate constant is a measure of the effectiveness of the catalyst. Comparison with previous data indicates that the rates of conversion of Velva lignite and of Rock Springs coal were about equal when no catalyst was added, as shown in

figure 9. Tin and molybdenum were about equally effective in increasing the rates of conversion of Velva lignite which were, however, much lower than those for the conversion of Rock Springs coal. Higher pressures increased the effectiveness of these catalysts on the conversion of Rock Springs coal more than on that of the lignite.

Nickelous chloride impregnated on coal had shown considerable promise as a hydrogenating catalyst, and the investigation of nickel compounds was continued under a cooperative agreement between the Bureau of Mines and the International Nickel Co. Nickelous sulfate was studied because it is the cheapest nickel salt and because the chloride produced hydrogen chloride, which is corrosive. In runs on Rock Springs coal at 400° C., the reaction rate was initially quite rapid, exceeding the rate for molybdenum at low pressures and that for tin at all pressures. After about 20 minutes the reaction decreased and then proceeded at a slow rate. The catalyst may have been poisoned or changed to a less active form. Further investigation is in progress.

Development of Vapor-Phase Catalysts

Production of gasoline from coal by the conventional German process involves two operations, a primary liquefaction and a vapor-phase hydrogenation of the resulting middle oil to gasoline. The previous annual report described development of a catalyst equivalent to the satisfactory German catalyst, K-536. The catalyst produced in this laboratory was prepared by treating bentonite clay with hydrofluoric acid; impregnating the clay with ammonium sulfomolybdate, chromic acid, and zinc oxide; and mixing the clay with flowers of sulfur. The approximate concentration of molybdenum was 1 percent, chromium 2 percent, zinc 3.5 percent, and sulfur 7 percent.

More recent work was devoted to elucidating the roles of the components. Tests at 500° C. and hydrogen pressures of 8,600 p.s.i.g. with Filtrol-SR, activated alumina, and Davison silica-alumina cracking catalyst showed that all three have little refining activity; that is, they do not eliminate sufficient oxygen, sulfur, and nitrogen, which are present in the feed oil. Filtrol shows better cracking activity than either activated alumina or silica-alumina, as judged by the amount of gasoline made. Treatment of Filtrol-SR with hydrofluoric acid did not produce any improvement in refining or cracking.

Zinc or chromium, added in the specified amounts to hydrofluoric acid-treated Filtrol, had no discernible effect. Sulfur had a slight effect, producing a little higher yield of slightly more saturated gasoline and total oil. Molybdenum had a decided effect, producing 62.1 percent gasoline based on feed as compared with only 33.6 percent when Filtrol was used alone. Oxygen and sulfur were almost completely eliminated, and nitrogen was reduced to a very low value. However, too much saturation was obtained, as evidenced by the high hydrogen content of the product and the consequently much lower octane number of the gasoline (motor method 76.7 as against 89.8 for Filtrol alone).

A continuous distillation column was built to provide a method for distilling the product and obtaining the oil that is heavier than gasoline as recycle stock. This column was tested over a 16-hour period. Excellent control and material balances were obtained.

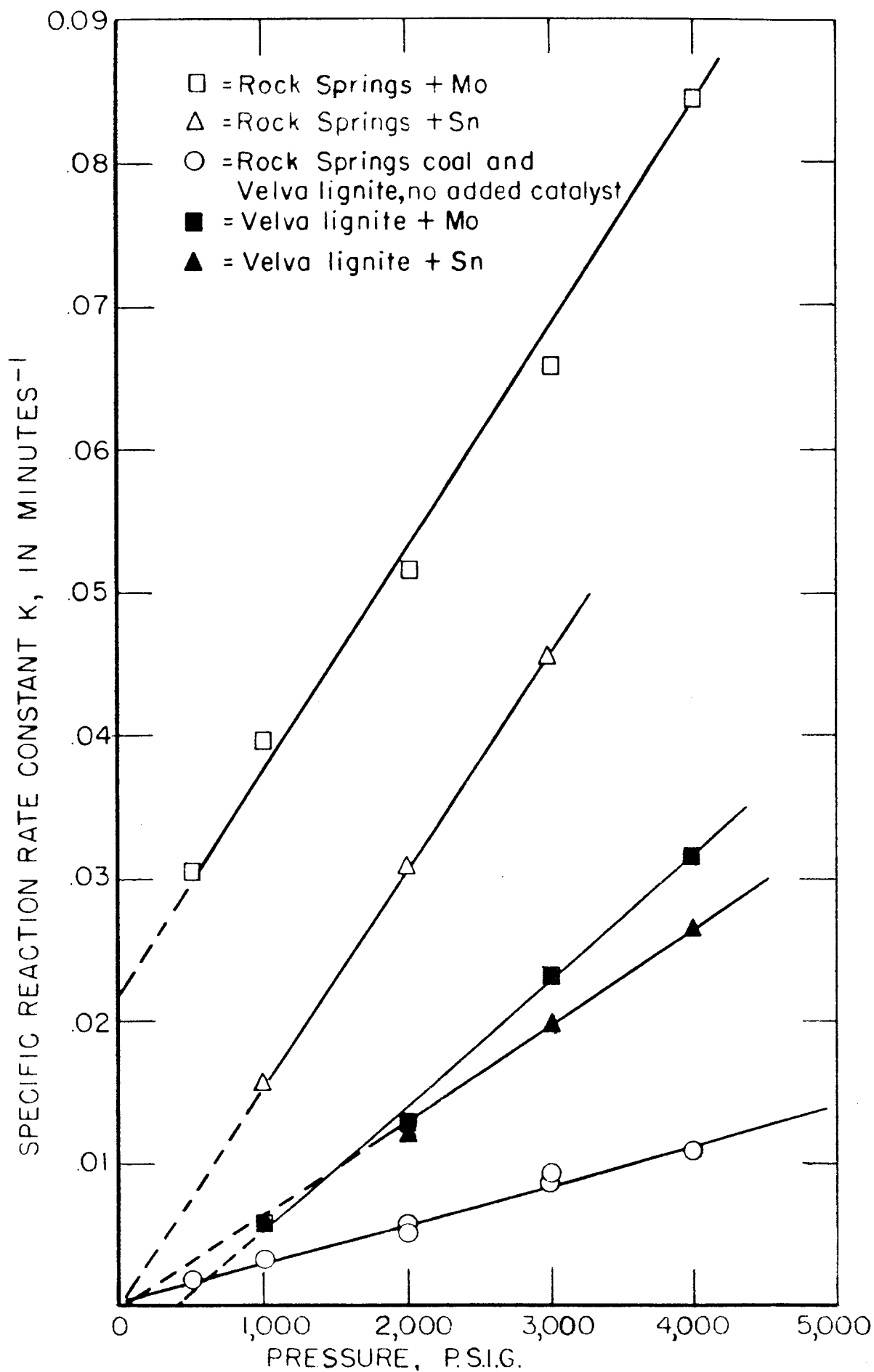


Figure 9. - Effect of pressure on specific rate constant.