

Bench-scale investigation was continued to determine equilibrium pressures of hydrogen sulfide and carbon dioxide over hot solutions of potassium carbonate containing various concentrations of these two gases. During the past year emphasis has been placed on pilot-plant operations to determine the extent to which hydrogen sulfide can be removed without affecting the steam consumption for regeneration. Selection of optimum operating conditions may permit elimination of iron oxide boxes to remove the final traces of hydrogen sulfide.

Because carbonate solutions are corrosive, a program is underway to determine the extent of their attack on various metals and the degree to which common inhibitors will eliminate such chemical action. Attack by uninhibited carbonate solution, acidified with carbon dioxide to a carbonate-bicarbonate ratio of 0.34, resulted in severe metal loss on both high- and low-carbon steel. Brass and stainless steel were relatively unaffected. Results of tests with unacidified solutions were similar for each metal tested, except that the degree of attack was much less severe.

Removal of Dust

Dust must be removed from the gas stream entering a fixed catalyst bed to avoid loss of catalytic activity. Tests have shown that accumulation of dust in the bed decreases the available surface area of the catalyst. Periodically a mass of dust may break loose and pass through the bed, restoring the activity, in part. Little or no dust penetration into the surface of catalyst pellets has been found.

The effect of dust depends both on its concentration and on its size distribution. Methods are being developed for generating hot dust-laden gas, for sampling that will not cause agglomeration of dust particles and thus false size distributions, and for removing dust at elevated temperatures and pressures. For sampling a fine wire-mesh filter has been found satisfactory. Studies are underway to develop a high-temperature electrostatic precipitator. Theoretical considerations indicate that a magnetic field superimposed upon the electrostatic field in the precipitator should improve the removal of dust at elevated temperatures, and this possibility is being investigated.

Process Economics

As a guide for its research programs, both completed and underway, the Bureau makes cost studies of the processes and unit operations involved. Two were published this year.^{71 72/}

71/ Katell, Sidney, and McGee, J. P., An Economic Study of Air Compression Costs: Cost Engineering, vol. 2, January 1957, pp. 5-9.

72/ Katell, Sidney, and Faber, John, An Economic Evaluation of Cooling Water Costs: Cost Engineering, vol. 2, No. 3, July 1957, pp. 70-76.

COMPLETE CONVERSION OF COAL TO FLUID FUELS

Coal Hydrogenation

Autoclave Studies

The mechanism of the iron-catalyzed hydrogenation of coal was studied in a rotating batch autoclave at 450° C. and hydrogen at 8,000 p.s.i. (fig. 18). Experiments were conducted with a paraffinic vehicle (n-octadecane), with coal-hydrogenation oil, and in the absence of any vehicle. Catalysts used were metallic iron and six iron compounds. Addition of hydrogen sulfide markedly increased the catalytic activities of all catalysts except iron chloride and sulfide. Ferrous sulfide may be the effective catalyst in all instances. Unlike the other catalysts, ferrous chloride may operate by a different mechanism. Considerably more liquefaction of coal was obtained with a coal-hydrogenation vehicle oil than with the paraffinic vehicle or in the absence of a vehicle. Work is also in progress on iron catalysts impregnated on either coal or an inert support, such as graphite.

Preliminary results on the iron-catalyzed hydrogenation of asphaltene indicate that the iron chlorides have a unique activity among iron catalysts in this reaction. The mechanism may involve homogeneous catalysis by dissolved ferrous chloride.

A study has been made of the hydrogenolysis of phenyl ether at 400° C. and 500 atmospheres of hydrogen with ferrous sulfide, metallic iron, and ferrous chloride catalysts. Ferrous chloride was inactive for the hydrogenolysis of phenyl ether. Further studies of this nature are being made with benzyl and alkyl ethers.

The reaction of coal with ammonia was investigated at 400° to 500° C. and pressures up to more than 400 atmospheres. Nitrogen-containing organic compounds were formed, but ammonia did not cause any greater liquefaction of coal than was obtained by pyrolysis in an inert atmosphere.

Autoclave data indicated that high conversions of coal to a distillable oil with low asphaltene yields could be obtained in the pilot plant at about 460° C. and 2,500 p.s.i. in the presence of acid-promoted molybdenum catalyst, although the throughput would probably be lower than in commercial high-pressure processes.

Pilot Plant

Low-Pressure Hydrogenation

The advent of the industrial gas turbine and jet aircraft may cause a shift of demand from gasoline to higher boiling distillates, which may also be used eventually for domestic and industrial heating. Production of such distillates by hydrogenation in a single-stage, liquid-phase hydrogenation at low pressures would be more favorable economically than conventional hydrogenation as smaller quantities of hydrogen and simpler plants would be required.

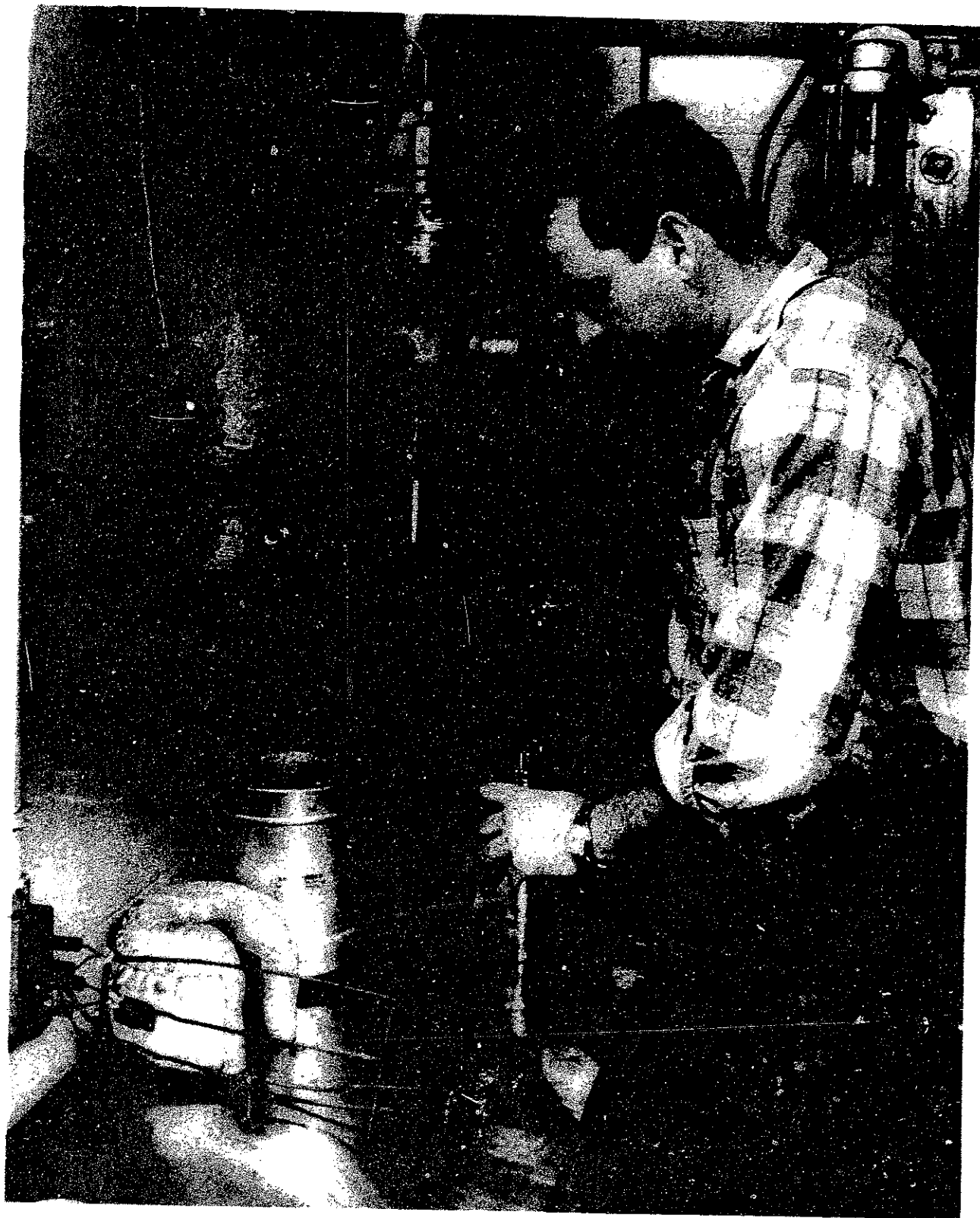


FIGURE 18. - Components of Autoclave for High-Pressure Reactions.

Because it was anticipated that the throughput at the lower pressure would be decreased, the existing high-pressure pilot plant was modified by installation of additional reactors (fig. 19). A program was developed to find the throughput and catalyst concentrations required for satisfactory conversion of coal

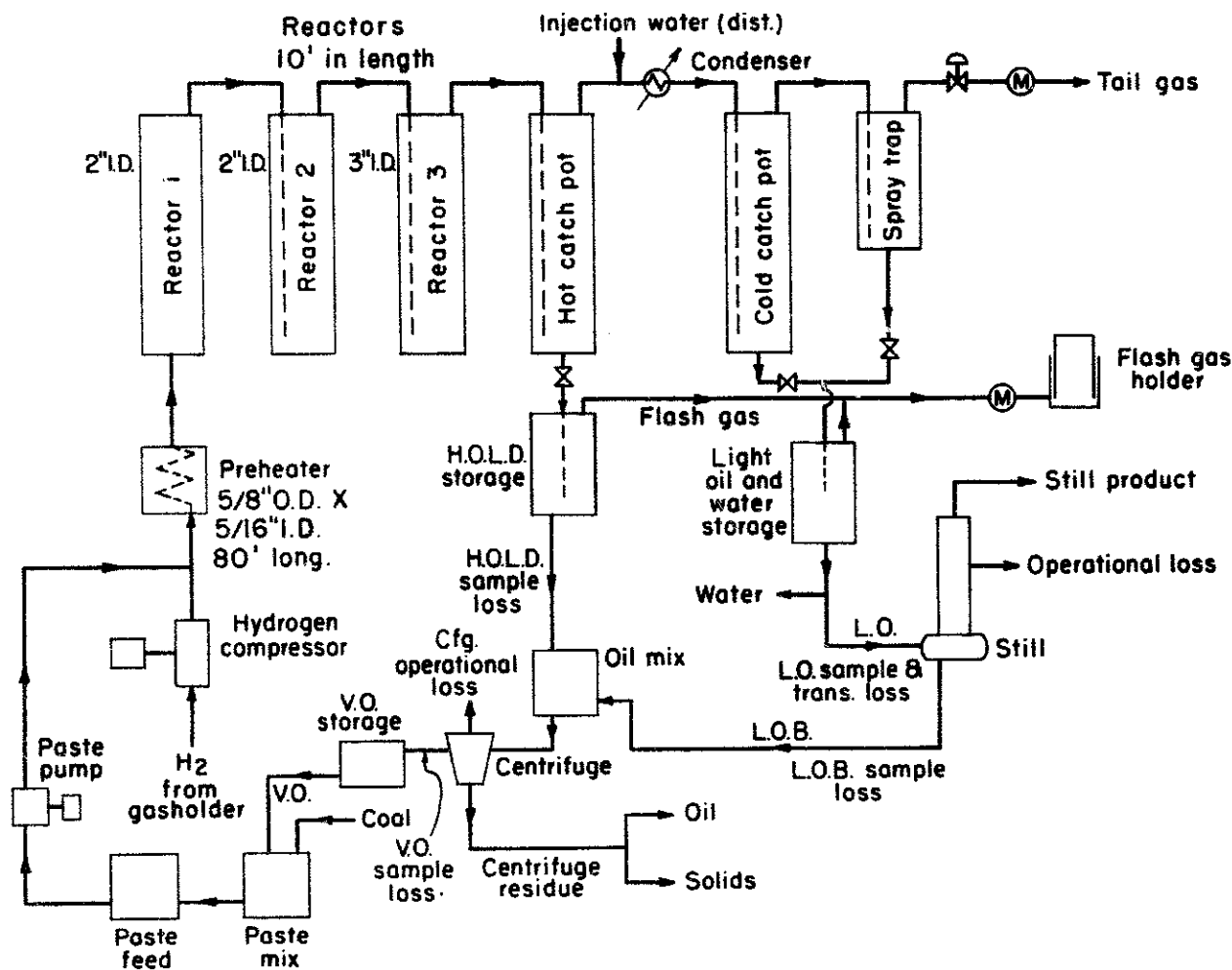


FIGURE 19. - Pilot Plant for Hydrogenating Coal at Relatively Low Pressures.

and primary coal-hydrogenation products at low pressures to appreciable yields of distillable oils with minimum production of gaseous hydrocarbons.

On completion of exploratory tests a study was made to determine the effect of throughput on product distribution at 2,000 p.s.i., 465° C., with 0.5 percent molybdenum (as ammonium molybdate) on coal at throughputs of 17.3, 21.5, and 24.1 pounds of coal per cubic foot of reaction space per hour. Operations with coal paste containing 40 to 45 percent coal were successful, and no difficulty was experienced in handling the high molecular products that were recycled with the fresh coal feed. The overall conversion of coal to liquid and gaseous products was 95 percent, regardless of throughput. The yield of liquid products increased only slightly as throughput increased, and the yield

of gaseous hydrocarbons decreased. The physical character of the recycle-oil stream was very sensitive to throughput. Virtually all of the ash was removed from the recycle stream with no difficulty, and adequate quantities of unreacted organic matter were removed to maintain a reasonably low steady-state burden of solids.

Efforts also were made to lower the concentrations of catalyst, because the use of 0.5 percent molybdenum on coal would be uneconomical without an efficient low-cost technique for recovering catalyst. Operation with 0.1 percent molybdenum was possible by reducing throughput to 14 pounds of coal per cubic foot of reaction space per hour, about one-half of the rate possible in 10,000-p.s.i. operations. Reduction in throughput resulted in a lower viscosity of the recycle stream, so that the solids could be removed by centrifugation. Results were similar to those obtained with 0.5 percent molybdenum at the higher throughput.

High-Temperature Hydrogenation

The production of high-B.t.u. gas by reacting hydrogen with coal at high temperatures has been investigated in several laboratories over the past 15 years. A review of these hydrocarbonization processes was published.^{73/}

The possibility of using very short reaction times at 800° C. for hydrogenating coal to low-boiling oils and gaseous hydrocarbons in a once-through operation was investigated in a semicontinuous unit. Studies were made with Rock Springs, Wyo., coal (bituminous C) to determine the effect of residence time at 800° C. and 6,000 p.s.i.g.^{74/} At a residence time of 1 minute and with 1 percent molybdenum (as ammonium molybdate) on coal 48 percent of the coal was converted to gaseous hydrocarbons and about 10 percent to aromatic oils. With a retention time of 15 minutes, the yield of gaseous hydrocarbons increased to 69 percent, but the yield of oil remained constant. In all cases 90 volume-percent of the hydrocarbon gases was methane and about 10 percent ethane. In the absence of a catalyst the yields of gaseous and liquid products decreased substantially at a residence time of 1 minute, but they were unchanged at a retention time of 15 minutes. A small continuous unit for hydrogenating dry coal is being constructed.

Characterization of Hydrogenation Products

Mass-spectrometric analysis of liquid coal-hydrogenation products has been extended by using a low-ionizing voltage. By this method, the types of compounds present and the molecular weights of the hydrocarbon homologs can be determined simply by inspecting the mass-spectrometer chart. These data combined with a quantitative type analysis provide a rapid method for investigating

^{73/} Newman, L. L., and Pipilen, A. P., Hydro-Carbonization of Coal for High B.t.u. Gas. Part I: Gas Age, May 16, 1957, pp. 16-21; Part II. Gas Age, May 30, 1957, pp. 18-20, 44.

^{74/} Hiteshue, R. W., Anderson, R. B., and Schlesinger, M. D., Hydrogenating Coal at 800° C.: Ind. Eng. Chem., vol. 49, No. 12, December 1957, pp. 2008-2010.

complex, high-boiling, coal-hydrogenation fractions. The low-ionization-voltage method has been shown to be valuable in characterization of the phenolic constituents of coal-hydrogenation products and of low-temperature tar.

For characterization of synthetic fuels, new techniques of gas chromatography have been developed. With suitable liquid substrates, complicated mixtures can be separated. Other developments include the use of molecular sieves to separate branched from straight-chain isomers, the use of silver salts and ethylene glycol to separate olefins, and the preparation of trimethylsilyl ethers to aid in identifying alcohols. Chromatographic apparatus that can be used for materials with boiling points up to 450° C. has been developed for operation at 300° C. The use of rhenium as an electron emitter for mass-spectrometer ion sources has resulted in greater stability and more efficient use of the instrument for analyzing samples containing high percentages of aromatic compounds, such as coal-hydrogenation products.

Fischer-Tropsch and Related Syntheses

An alternative to the coal-hydrogenation method for producing synthetic liquid fuels involves intermediate gasification of coal to a synthesis gas containing carbon monoxide and hydrogen, with subsequent conversion to liquid products by catalytic reactions.

Chemistry of Metal Carbonyls

Investigations in carbonyl chemistry have elucidated the structure of a number of unusual compounds, many of which are similar to intermediates that have been postulated in the Fischer-Tropsch synthesis. A major aim of this work during the past year has therefore been to determine the manner in which new carbon-to-carbon bonds are formed in reactions catalyzed by complexes of iron and cobalt. A study of the cobalt carbonyl and iron carbonyl-catalyzed addition of CO+H₂ to olefins has led to the conclusion that these reactions involve the formation of a complex between the olefin, binuclear metal carbonyls, and hydrogen.^{75 76 77/} This mechanism implies that substrate CO and H₂ are brought together on two metal atoms in a "surface complex" and that chain lengthening involves the three molecules gathered together in this fashion.

From a study of the reaction between dicobalt octacarbonyl with an acetylene the first direct proof was obtained that the addition of carbon monoxide

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- 75/ Wender, I., and Sternberg, H. W., Homogeneous Metal Carbonyl Reactions and Their Relations to Heterogeneous Catalysis: *Advances in Catalysis*, vol. 9, 1957, pp. 594-608.
- 76/ Sternberg, H. W., Markby, R., and Wender, I., Binuclear Iron Carbonyls and Their Significance as Catalytic Intermediates: *Jour. Am. Chem. Soc.*, vol. 79, No. 23, Dec. 5, 1957, pp. 6116-6121.
- 77/ Greenfield, H., Wotiz, J. H., and Wender, I., Reactions of Acetylenic Compounds Under Hydroformylation Conditions: *Jour. Org. Chem.*, vol. 22, No. 5, May 1957, pp. 542-546.

to a substrate can proceed via a complex.^{78 79/} Data were also obtained supporting the inference that complexes involving more than two metal atoms lead to the high-molecular-weight products obtained in some types of Fischer-Tropsch reactions. Furthermore, the first clear evidence that an aromatic compound can be formed by the catalytic action of a metal carbonyl was found.

Catalyst Studies

In studies of catalysts in the Fischer-Tropsch synthesis it has been shown, by measurements of surface area and pore volume, that the geometry of the catalysts changes during pretreatment and synthesis. After synthesis, iron catalysts have low surface areas and pore volumes, resulting partly from formation of iron oxide during the synthesis and partly from deposition of wax in the pores of the catalyst. That the mechanism of the synthesis involves absorption of gas in liquid hydrocarbons in catalyst pores and diffusion of this gas to the catalyst surface is supported by values of diffusivity determined from analysis of data obtained in studying the activation energies as a function of particle size of the catalyst. The physical and chemical nature of iron catalysts is considerably altered by wax and carbon deposition and by formation of carbides and magnetite.^{80 81/}

The Bureau has investigated the changes in the surface areas and pore volumes of iron catalysts resulting from varying the sequence of oxidation, reduction, carburizing, and nitriding and from subsequent use in the synthesis itself. Nitrided catalysts acquire appreciable amounts of carbon and become iron carbonitrides after a short period of operation.^{82/}

Various forms of catalyst have been studied for the hot-gas-recycle process, which requires a catalyst with a high surface-volume ratio and a minimal resistance to the flow of gases. Pretreated sheet-steel catalysts have been developed that have a low but satisfactory activity, although disintegration of the catalyst surface during a test proved to be troublesome. Some progress has been made in preparing and stabilizing the surface. The activity of such catalysts is confined to a thin layer, possibly only a few hundredths of a millimeter thick, so that most of the material is making little or no contribution to the overall catalytic activity.

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- ^{78/} Wender, I., Sternberg, H. W., Metlin, S., and Orchin, M., Dicobalt Octacarbonyl: Inorganic Syntheses, McGraw-Hill Book Co., Inc., New York, N. Y., vol. 5, 1957, pp. 190-192.
- ^{79/} Sternberg, H. W., Wender, I., and Orchin, M., Cobalt Tetracarbonyl Hydride (Cobalt Hydrocarbonyl): Inorganic Syntheses, McGraw-Hill Book Co., Inc., New York, N. Y., vol. 5, 1957, pp. 192-195.
- ^{80/} Stein, K. C., Thompson, G. P., and Anderson, R. B., Iron Catalysts and the Fischer-Tropsch Synthesis: Ind. Eng. Chem., vol. 49, No. 3, March 1957, p. 410.
- ^{81/} Stein, K. C., Thompson, G. P., and Anderson, R. B., The Fischer-Tropsch Synthesis. XVII. Changes of Iron Catalysts During Pretreatment and Synthesis: Jour. Phys. Chem., vol. 61, 1957, pp. 928-932.
- ^{82/} Shultz, J. F., Abelson, M., Shaw, L., and Anderson, R. B., Fischer-Tropsch Synthesis. Nitrides and Carbonitrides of Iron as Catalysts: Ind. Eng. Chem., vol. 49, No. 12, December 1957, pp. 2055-2060.

Sulfur Poisoning

Studies have been made of the poisoning of an iron catalyst by adding sulfur compounds to synthesis gas - gas-phase poisoning - and by pretreating the catalyst in a solution of the compound prior to its use - liquid-phase poisoning. The compounds studied have included hydrogen sulfide, sulfur dioxide, carbon oxysulfide, and carbon disulfide. The poison absorbed from the gas phase was 20 or more times as deleterious as that from the liquid phase; 0.1 mg. or less reduced the activity 50 percent.

Pilot Plant

In the hot-gas-recycle method of Fischer-Tropsch synthesis the large exothermic heat of the reaction is absorbed by large volumes of gas circulating through the reactor in direct contact with the catalyst. With this reactor, no heat-exchange surface is necessary in the catalyst bed, simplifying construction and decreasing the cost of reactors (fig. 20). The sensible heat of the recycle

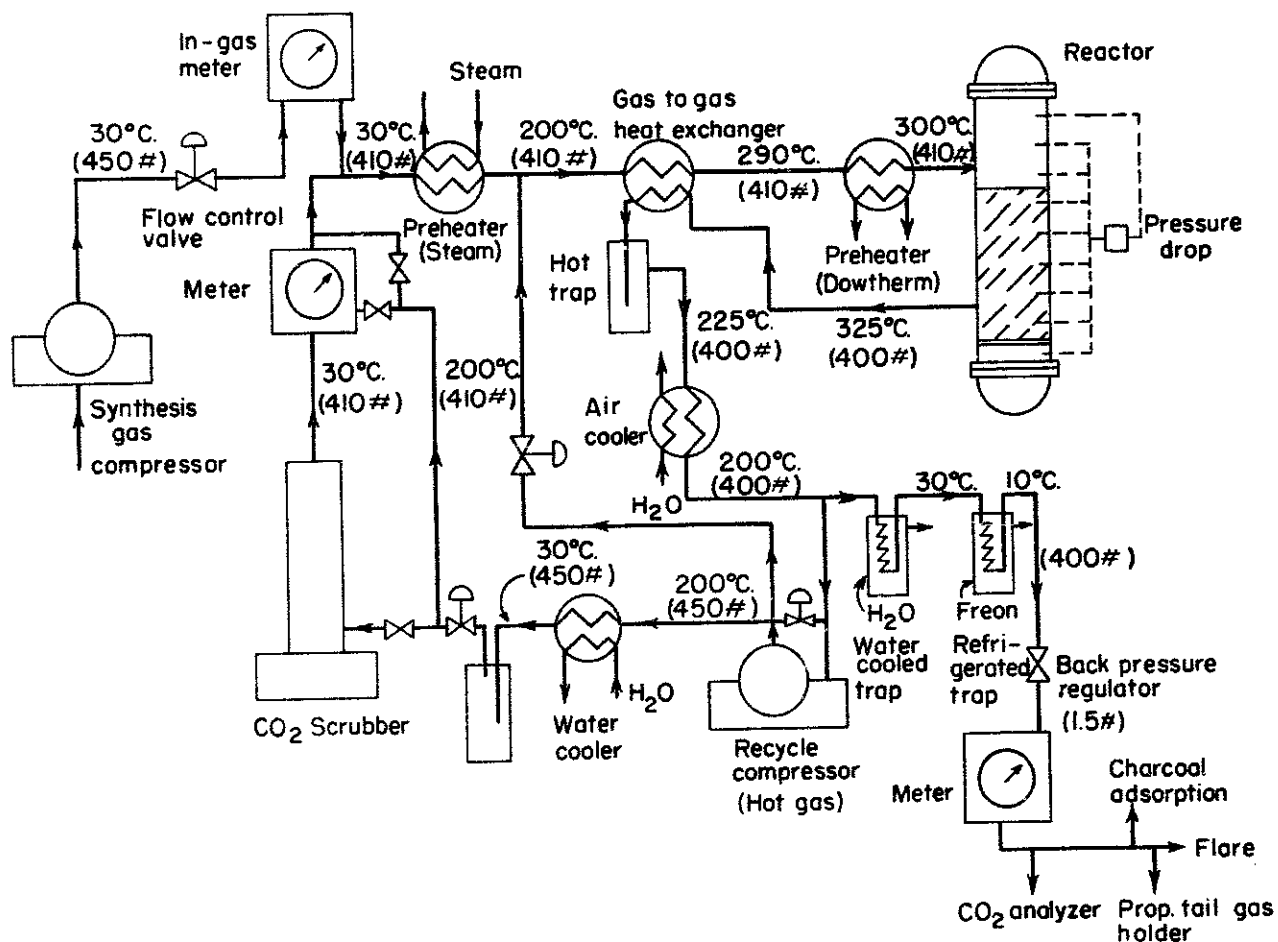


FIGURE 20. - Pilot Plant for Fischer-Tropsch Synthesis by Hot-Gas-Recycle Process.

gas is removed by generating high-pressure steam in an external waste-heat boiler. In addition, this system can be operated readily at high temperatures, where high productivity of gasoline can be obtained. Special fixed catalyst beds are needed to maintain a low pressure drop, as the cost of recycling the gas would be excessively high with beds of granular catalyst.

The hot-gas-recycle process was operated for 85 days during the year with a few mechanical difficulties. For more than half of this time conversion of 90 to 93 percent of a feed gas containing 1.3 H₂+1 CO was achieved at an hourly space velocity of 1,000. The catalyst was prepared from lathe turnings of 1018 carbon steel; its activity remained constant through most of the test. The pressure drop across the bed was low, increasing slowly from 1 to 1-1/2 p.s.i. per foot of bed. Temperature control was excellent and there was no evidence of overheating the catalyst. During the operation, 190 pounds of hydrocarbon product (C₃+) was made per pound of iron catalyst. The experiment ended after 2,000 hours, when a leak developed in the cylinder head of the recycle compressor. Although the experiment was made at high temperatures (300° to 320° C.) and high space velocities to increase gasoline production and throughput, this type of reactor can obviously be operated at lower temperatures. During the year, a summary of the oil-circulation Fischer-Tropsch process has been published.^{83/}

Characterization of Synthesis Products

Gas-chromatography techniques have been applied to the study of selected light fractions of Fischer-Tropsch products that were prepared under many conditions. The results agree with the mechanism of chain growth previously developed in Bureau laboratories.

Correlation of mass spectra with molecular structures continued for various types of compounds present in Fischer-Tropsch product. Mass spectra were published of 26 aliphatic trimethylsilyl ethers used in analyzing alcohols.^{84/} Correlation studies have also been completed on the mass spectra of 31 aliphatic esters.

Researchers have investigated a liquid Fischer-Tropsch product boiling above 100° C. both by room-temperature and high-temperature mass spectrometers. Complete carbon-number distributions have been obtained for straight-chain paraffins, olefins, ketones, and alcohols having 2 to 22 carbon atoms per molecule.

By means of molecular-sieve techniques the ratio of branched to straight-chain hydrocarbons has been determined in a fraction consisting primarily of

^{83/} Benson, H. E., Field, J. H., Bienstock, D., Nagel, R. R., Brunn, L. W., Hawk, C. O., Crowell, J. H., and Storch, H. H., Development of the Fischer-Tropsch Oil-Recycle Process: Bureau of Mines Bull. 568, 1957, 72 pp.

^{84/} Sharkey, A. G., Jr., Friedel, R. A., Langer, S. H., Mass Spectra of Trimethylsilyl Derivatives: Anal. Chem., vol. 29, No. 5, May 1957, pp. 770-776.

C₁₃ and C₁₄ hydrocarbons. Results show the sample to be 1/3 by volume normal hydrocarbons, which fact agrees with values predicted by the Fischer-Tropsch chain-growth scheme.

Reviews of Literature

In connection with the Bureau's studies of the Fischer-Tropsch and related processes a book review and four contributions to reference works were published.85 86 87 88 89/

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- 85/ Hofer, L. J. E., Advances in Catalysis and Related Subjects, vol. 8: Book Review, Jour. Am. Chem. Soc., vol. 79, No. 7, Apr. 5, 1957, p. 1774.
- 86/ Cohn, E. M., Fischer-Tropsch Process: The Encyclopedia of Chemistry (George L. Clark and Gessner G. Hawley, editors), Reinhold Pub. Corp., New York, N. Y., 1957, pp. 397-398.
- 87/ Hofer, L. J. E., Carbides: The Encyclopedia of Chemistry (George L. Clark and Gessner G. Hawley, editors), Reinhold Pub. Corp., New York, N. Y., 1957, pp. 165-168.
- 88/ Wender, Irving, and Orchin, Milton, Reactions of Carbon Monoxide: Catalysis, Reinhold Pub. Corp., New York, N. Y., vol. 5, ch. 1, 1957, pp. 1-72.
- 89/ Wender, Irving, Sternberg, H. W., and Orchin, Milton, The Oxo Reaction: Catalysis, Reinhold Pub. Corp., New York, N. Y., vol. 5, ch. 2, 1957, pp. 73-130.