

remaining. In an associated study of the effect of variable contact time on hydrogenation of uncatalyzed subbituminous C coal, most of the conversion at the temperatures and pressures studied was found to occur within 0.12 minute and to approach a maximum in about 3 to 6 minutes.

Process Development

A series of pilot-plant experiments furnished data on variables in hydrogenation, such as kind of coal, catalyst, residence time, pressure, and temperature. For example, in hydrogenation of the same subbituminous C coal at 440° C. and 3,500 p.s.i. with 0.1 percent stannous sulfide plus 0.05 percent iodoform as catalyst, reducing residence time from 0.9 to 0.2 hour increased the yield of oil from 15 to 70 pounds per hour per cubic foot of reaction space.

Catalysts were tested with this coal at 460° C. under recycle pasting-oil conditions. At 3,500 p.s.i. of hydrogen, 0.1 percent tin as stannous sulfide plus 0.5 percent ammonium chloride, 0.5 percent nickel as nickelous chloride, or 1.0 percent iron as ferrous sulfate, all converted coal to liquid and gaseous hydrocarbons at essentially the same rate, with either 0.4- or 0.9-hour residence time. At 1,500 p.s.i., however, conversion was least with 1.0 percent iron as ferrous sulfate or 1.0 percent nickel as nickelous chloride and greatest with 0.5 percent tin as stannous chloride or 0.5 percent molybdenum as ammonium molybdate. Hydrogenation at 1,500 p.s.i. apparently would be feasible for production of fuel oil, provided active catalysts such as tin or molybdenum were used.

High-Temperature, One-Step Hydrogenation. - Another group of experiments dealt with the possible high-temperature hydrogenation of coal into refined gasoline in a single step. Autoclave and bench-scale experiments had suggested the possibility of such single-step conversion, provided high enough temperatures, large quantities of active catalysts, and appropriate throughputs could be utilized without incurring "coking." In pilot-plant tests, at 8,000 p.s.i. and with 1 percent molybdenum catalyst, reactor temperature could be controlled adequately around 450° C. by admitting cold hydrogen; but control was not possible at temperatures above 480° C. due to runaway temperatures.

The results indicated the need of moderating the reaction by using less reactive coal or by lowering the catalyst concentration. In further tests (with only 0.01 percent molybdenum catalyst) temperature control was comparatively good at 480°, 500°, and 525° C. Conversion to liquids and gases was 93 percent at 480° C. and about 88 percent for the two higher temperatures. However, in these tests, as with 0.1 percent of molybdenum, "coking" gave serious difficulty.

Catalyst Development for Vapor-Phase Hydrogenation. - German catalyst K-536, developed for vapor-phase hydrogenation, was used in the Bureau's demonstration plant. This catalyst was reproduced in the laboratory and found to be as active as the German product. Tests of the separate constituents indicated that activity was due largely to molybdenum; the other constituents improved the selectivity of the catalyst.

Hydrocarbonization. - In hydrocarbonization coal is carbonized in hydrogen at moderate pressures. Subbituminous coal was converted to char, oil, and hydrocarbon gases in small-scale and pilot-plant experiments. Particularly in continuous operations, agglomeration of the char was troublesome. With rapid heating, mild agglomeration began at 500° C., and severe agglomeration occurred at 600° C. With slow or stepwise heating, however, coal was hydrocarbonized at temperatures as high as 700° C. without agglomeration.

Hydrogenation Demonstration Plant

The coal-hydrogenation demonstration plant, built to furnish engineering information on the design and operation of large-scale hydrogenation units, was operated from 1949 to 1953. Special problems in design and construction of this 200-barrel-per-day plant included selection of suitable alloy steels and of high-pressure vessels, injection pumps, tubing, and valves for use at 700 atmospheres (10,300 p.s.i.).

Six coals were processed, ranging in rank from lignite to high-volatile-A bituminous. Of the 1.5 million gallons of gasoline produced, 1 million was fleet-tested by the armed services. This 78-octane (motor method, unleaded) synthetic gasoline was found equal to petroleum gasoline.

During design and operation of the plant information was developed on heat, power, and other requirements for hydrogenation. Although estimates indicated that 55 percent of the B.t.u.'s in the total coal used for power and processing might be available in the liquid product, such efficiency has not been achieved in any coal-hydrogenation plant. From practical experience not over 45 percent thermal efficiency can be expected.

Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis is a process for making synthetic liquid fuels by hydrogenating carbon monoxide on catalysts such as iron, cobalt, and nickel.

Basic Research

Fischer had suggested that carbides of the metals are intermediates in this reaction. However, work by the Bureau of Mines and elsewhere showed that bulk nickel carbide and cobalt carbide catalyzed the reaction only slightly, if at all, although iron carbides were active. Nitrides and carbonitrides of iron were discovered to be active catalysts with long life, yielding a product with large amounts of alcohols.

Pore Geometry of Catalysts. - Experiments on cobalt-thoria-kieselguhr catalysts suggested that kieselguhr acted chiefly to produce and maintain a structure of high pore volume. Data obtained before, during, and after 12 weeks of synthesis indicated that surface area and pore volume had not changed. When a fused iron oxide catalyst was reduced in the range of 400°-600° C., the surface area increased linearly at a given temperature up to about 90-percent reduction. At 450° C. the average pore diameter varied from 300-350 A. and increased

slightly near 100-percent reduction. Massive iron catalysts, prepared by oxidation of suitable forms of iron or steel, such as lathe turnings or steel wool, had porous outer layers with surface areas of about 4 m.² and pore volumes of 0.070 ml. per gram of active layer.

Kinetics and Mechanism of the Fischer-Tropsch Synthesis. - The rate of synthesis over cobalt on kieselguhr was approximately independent of pressure between 1 and 7.8 atmospheres, in experiments in which pressure was increased during operation with the same charge of catalyst; decreasing pressure during operation with a particular charge of catalyst strongly diminished the activity. Apparent overall activation energies for synthesis on cobalt were about 25 kilocalories per mole at atmospheric pressure, and 20 at 7.8 atmospheres. For iron catalysts, these energies varied from 19 to 21 kcal. per mole.

Studies of the mechanism of growth of organic compounds in synthesis suggested a mechanism involving absorbed oxygenated intermediates on the catalytic surface. The detailed mechanism was postulated on the assumption that (a) hydrogen is adsorbed atomically on metal atoms, (b) carbon monoxide is chemisorbed with carbonyllike bonding on metal atoms, and (c) the adsorbed carbon monoxide is partly hydrogenated. Equations were proposed for growth and termination of carbon chains to yield aldehydes, alcohols, olefins, and paraffins and for producing acids and esters. These postulates also accounted for the size, configuration, and relative abundance of compounds obtained.

Chemistry of Carbonyls. - The reaction of carbon monoxide and hydrogen with an olefin, with cobalt carbonyl as catalyst (the oxo or hydroformylation reaction), was studied as a homogeneous counterpart of the heterogeneous Fischer-Tropsch synthesis. The oxoreaction was considered to involve formation of a cobalt carbonyl-olefin complex, reduction by hydrogen to a hydrogenated complex, decomposition of this complex to the corresponding aldehydes and $\text{Co}_2(\text{CO})_6$, and regeneration of dicobalt octacarbonyl by reaction with carbon monoxide.

Preparation, Pretreatment, and Testing of Fischer-Tropsch Catalysts

Extensive evaluations of catalysts were carried out in a standardized apparatus which provided comparable data rather than necessarily maximum yields. With cobalt catalysts data were obtained on the value of various kieselguhrs, on the effect of pelleting, and on the activity of carburized cobalt. With iron, inactivity of catalysts prepared from solutions of ferric chloride probably resulted from poisoning by residual chloride. Alkali was the only chemical promoter for iron catalysts; however, structural promoters were needed to retain porosity and surface area.

The methods of pretreating iron catalysts, such as carbiding, nitriding, and carbonitriding, frequently caused large changes in activity and selectivity. A surprising discovery was that iron nitrides and carbonitrides were active and stable in the Fischer-Tropsch synthesis and produced exceptionally high yields of oxygenated compounds.

Process Development

The industrial Fischer-Tropsch process in Germany was characterized by low productivity per unit volume of catalyst space; expensive, complex reactors; and inflexibility of operating conditions and hence of types of products made. The Bureau of Mines attempted to overcome these disadvantages by new process development, primarily of the oil-circulation and slurry processes.

Oil-Circulation Process. - In the oil-circulation process cooling oil was trickled over the catalyst bed, and the heat of reaction was removed at first by vaporizing the oil. Later the bed was completely submerged in oil, and the heat of reaction was removed as sensible heat of the circulating oil. In experiments with $1\text{H}_2:1\text{CO}$ the iron particles cemented together, and the increased pressure drop across the catalyst compelled termination of the synthesis after 1 to 3 months, although the catalyst was still active. With a hydrogen-rich gas, $1.3\text{H}_2:1\text{CO}$, there was less difficulty. When the flow of oil was increased enough to expand the catalyst bed 10 to 20 percent above its settled height and to produce slow movement of the catalyst particles, catalyst cementation and the resultant increased pressure drop were eliminated.

Expanded beds of fused-iron oxide catalyst were used in a 1-barrel-per-day pilot plant and in the 40-barrel-per-day demonstration plant. Higher space velocities and space-time yields, based on reactor or catalyst volume, were obtained with the expanded beds than with fixed beds. With both operations yields of C_3+ hydrocarbons ranged from about 150 to 175 grams per cubic meter of $\text{H}_2 + \text{CO}$ converted. About 50 to 65 percent of this C_3+ product was in the gasoline range.

To improve the flexibility of the oil-circulation process and to permit operation at high temperatures, at which fused-iron oxide catalysts disintegrated, trials were run with more durable catalysts of activated iron or steel lathe turnings and 1/8-inch-diameter steel shot. These massive catalysts operated successfully at 270° to 290°C . Lathe turnings resisted disintegration and oxidation and maintained activity for long periods. For example, one catalyst operated continuously without difficulty for over 2,700 hours, including 1,200 hours at or above 290°C . At 283°C ., 85 percent of the C_3+ product boiled in the gasoline range.

Development of the oil-circulation process on a small scale is considered virtually completed. Internal cooling by oil circulation has been shown to be practical and versatile, as distribution of products can be varied over a relatively wide range.

Slurry Process. - In the slurry process finely ground catalyst particles are held in suspension in a high-boiling oil by gas agitation or by circulation of the slurry. Large units are cooled by a system of internal bayonet tubes or by circulating the slurry through an external heat exchanger. A small pilot plant was constructed with a 3-inch-diameter reactor holding a 10-foot height of slurry or about 15 liters (4 gallons).

In initial experiments with precipitated-iron catalysts, 65 to 80 percent of the gas was converted at about 270° C., 100 to 300 p.s.i., and hourly space velocities of 100 to 300 volumes of gas per volume of slurry in the reactor. Alan Wood magnetite ore and fused iron oxide were the most promising other catalysts tested. Operable ranges of variables included catalyst concentrations of 50 to 500 grams of iron per liter of slurry, ratios of synthesis gas as produced most easily by gasification of coal (0.7:1 to 1.3:1 of H₂:CO), pressures of 300 to 400 p.s.i., and a wide range of space velocities; additives helped to keep catalyst particles suspended. Gasoline yield with the slurry process was as high as 89 percent of the C₃₊ product.

Iron catalyst could be reduced with hydrogen and nitrified with ammonia either directly in the slurry or in a separate dry bed unit. The catalyst proved stable and active. Of the condensed product, 60 to 70 percent was oxygenated chemicals. Nitrified catalysts are thus a means of converting coal to aliphatic oxygenated chemicals, predominantly alcohols.

Fischer-Tropsch Demonstration Plant

The demonstration plant was operated from 1951 to 1953. Based on pilot-plant experience, the synthesis was run with an oil-immersed, expanded bed of 4- to 10-mesh catalyst particles, and about 0.8H₂:1CO fresh gas. The catalyst was made by fusing millscale with small quantities of magnesia and potash.

In four runs more than 40,000 gallons of liquid products was obtained. Conversion of H₂ + CO exceeded 90 percent in parts of the final run. Difficulty was experienced because of disintegration of the catalyst, and the presence of up to 25 weight-percent of fines in the coolant oil made the process a combination slurry-expanded bed operation. Catalyst fines in the oil damaged pumps and necessitated frequent repairs. More recent improvements in Fischer-Tropsch catalyst, and redesign of the gas-inlet system of the reactor, might have circumvented these difficulties.

Problems and Outlook

Research under the Synthetic Liquid Fuels Act, in line with prior knowledge, has shown the feasibility of gasifying coal and of producing synthetic liquid fuels from coal either by direct hydrogenation or by the Fischer-Tropsch synthesis. Much new knowledge has been acquired in these fields, ranging from fundamental chemical data to building and operating large equipment of a kind not previously used in the United States. Although both processes consume more than half of the heating value of the total coal used in processing and supplying the energy for conversion, they are the only known methods by which substantially all the carbon in the processed coal is converted from a solid to a fluid fuel.

Gasoline made by these processes is still considered too expensive to compete with gasoline from petroleum at present. The cost of gasoline made from a Rock Springs, Wyo., subbituminous coal by either process has been estimated at around 18 cents per gallon, without allowance for interest, taxes, or profits and without credit for the value of byproducts. About 40 to 80 percent of this

cost represents the price of clean, compressed gas from coal. In addition to being affected by variations in the basic assumptions in such estimates, the costs for a particular plant would, of course, vary with local factors such as cost of coal, labor, housing, water, and transportation. (See chapter 8, especially tables 21 and 26.)

However, since supplies of crude petroleum and natural gas are not inexhaustible, provision should be made for the time when our vast coal reserves will have to supplement the natural fluid fuels. In the Bureau's continuing fundamental and applied research on synthetic fuel problems, more basic information is being sought about coal and its chemical behavior. Meanwhile, theoretical and practical studies are being made to reduce production costs by improving various stages in the processes or by developing new processes including a process for producing from coal a high-B.t.u. pipeline gas.

Combinations of conversion processes, perhaps in connection with carbonization, may contribute toward the economic feasibility of commercial synthetic fuel production. A flexible, integrated plant might thus emphasize production of different types of fluid fuels or byproducts under different economic conditions and even at different times of the year.