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DEVELOPMENT OF THE FISCHER-TROPSCH OIL-RECYCLE PROCESS

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Preface

One of the provisions of the Synthetic Liquid Fuels Act of 1944 (Public Law 290) authorized the Bureau of Mines to design, construct, and operate pilot plants for the production of synthetic liquid fuels from materials such as coal, oil shale, and agricultural and forestry products. Uncertainties concerning the availability of foreign sources of petroleum in international crises and the prospect of decreasing reserves within continental United States were strong arguments favoring this technologic undertaking.

This bulletin describes the development of an oil-recycle process on a small, pilot-plant scale for conducting the Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen mixtures (synthesis gas). Although synthesis gas can be readily produced from natural gas, coal or coallike substances would have to be considered the basic raw materials for a large-scale, synthetic-fuels industry, since they comprise over 95 percent of the fossil fuel-energy reserves of continental United States. Several other variants of this process are being investigated by the Bureau of Mines and by private industry, with private industry particularly active in developing fluidized-bed processes, such as that employed in a 6,000-barrel per day plant at Brownsville, Tex. As the cost of synthesis gas represents a major portion of the total cost of producing synthetic fuels, high conversion of this gas to the most valuable fuel, gasoline, is of utmost importance. A sound process evaluation can be based only on experimental data concerned with utilization of the synthesis gas, distribution of products, and operability of the process. The program of study for the oil-circulation process, carried out by the Gas Synthesis Section of the Synthetic Fuels Branch at Pittsburgh and Bruceton, Pa., has been pursued accordingly. The experimental results presented herein cover an 8-year period, 1943–51, during which time reports on portions of the work have been published.

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DEVELOPMENT OF THE FISCHER-TROPSCH OIL-RECYCLE PROCESS[1]

By

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Summary

THE FEASIBILITY of removing the heat of reaction from the catalyst by a cooling oil was first demonstrated in bench-scale tests. A flow of oil was trickled through the bed, and the heat evolved was dissipated by vaporization of the oil. This type of operation was used in early pilot-plant tests with cobalt and precipitated-iron catalysts. Better temperature control was achieved when the catalyst was completely submerged in the cooling medium rather than being only wetted. Use of cobalt was discontinued because of its high cost and relative scarcity, when considered for large-scale operation.

In submerged-bed operation, precipitated-iron catalysts disintegrated too rapidly and were replaced by fused catalysts of greater physical strength. Synthesis temperature and pressure were made independent of each other by using nonevaporative cooling instead of evaporative cooling, which depends upon vaporization of oil. Trouble-free operation and excellent temperature control were obtained with nonevaporative cooling of submerged beds of fused iron. However, a gradual increase in the pressure drop across the fixed bed occurred because the catalyst particles became agglomerated. This led to a further modification, "expanded-catalyst-bed" operation, in which the velocity of the cooling oil, flowing upward through the reactor, was raised enough to expand the catalyst bed about 5 to 30 percent above its settled height. Not only was cementation avoided, but the operating temperature was reduced 10° to 15° C. by using smaller catalyst particles with high surface areas. Lower temperatures contribute to attainment of longer catalyst life. The gas throughput was more than twice that of a fixed bed, based on the settled volume or weight of the catalyst.

Several experiments were conducted to study the effects of important variables upon conversion of synthesis gas, yield of products, and catalyst life. Results of these studies, details of the various phases of the pilot-plant development, and the characteristics of the synthesis products are described in this report. Of the products made in the latter part of this study, the blended gasoline (with 3 cc. of tetraethyl lead) had a research octane rating of 93.8, and the diesel oil had a cetane rating from 70 to 80.

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INTRODUCTION

The Fischer-Tropsch synthesis of liquid hydrocarbons by catalytic conversion of carbon monoxide and hydrogen is a strongly exothermic reaction, with about 7,200 B. t. u. evolved per pound of product. For this reason, and because of the relatively narrow range of allowable temperature gradient, the reactor must permit efficient heat transfer.

Since the synthesis was first disclosed by the Badische Anilin- und Soda-Fabrik (*3, 31, 32*)[a] in 1913, many types of reactors have been investigated, varying chiefly in their arrangements for removal of heat. Following fundamental laboratory studies by Fischer and Tropsch in Germany (*21*) and by other investigators in England (*19, 20*), France (*7*), Japan (*25*), and the United States (*24, 41*), Ruhrchemie constructed a fixed-bed pilot plant at Oberhausen-Holten, Germany, in 1933. Subsequently, several plants with a total capacity of 300,000 tons per year were built in Germany; and these were operated, during World War II, chiefly with a Co–ThO_2–MgO–kieselguhr catalyst at either atmospheric or medium pressure (10 atmospheres). To obtain the necessary heat transfer in these fixed-bed reactors, a large cooling-surface area had to be provided, and the maximum distance of any catalyst particle from a metallic heat-dissipating surface could not exceed 10 millimeters. The reaction heat evolved flowed through the metal wall to a surrounding cooling medium, usually water boiling under pressure. These reactors were complicated and expensive. The small gas throughput, hourly space velocities of 100 volumes of S. T. P. (see Glossary, p. 70) feed gas per hour per volume of catalyst, necessary to limit the rate of evolution of heat and thus maintain the low-temperature gradients requisite for acceptable yields increased the cost of operating the plants. A typical reactor operating at atmospheric pressure consisted of horizontal boiler tubes passing through vertical sheets (a modification of the "fin-tube principle") and had a total cooling surface of 43,000 sq. ft. Its over-all usable volume was about 650 cu. ft., and its production about 18 barrels of oil per day. In this reactor the catalyst was packed outside the tubes, in the spaces between the "fins." A double-tube pressure reactor of the same output capacity required approximately the same reaction volume but less cooling surface; the indication is that a somewhat greater over-all heat-transfer coefficient was attained. In this reactor the tubes were placed vertically, parallel to the gas flow. Each "tube" unit was made up of two concentric tubes, with the catalyst packed in the annulus between them.

In subsequent development considerable modifications were made in reactor designs and in modes of operation, primarily to attain better temperature control and to improve heat removal. Storch and associates (*44*) have discussed many of these various synthesis processes and listed them according to the following general categories:

1. Processes in which fixed beds of granular or pelleted catalysts are cooled by indirect heat exchange, with and without recycling of the tail gas.

As previously stated, the fixed-bed reactors were complex and limited in capacity. Low-temperature gradients at high conversions were difficult to attain and to maintain. Most of the reaction took place in those parts of the bed farthest removed from the heat-transfer surface; consequently, that is where most of the heat of reaction was liberated also, under conditions that favored localized high temperatures and poor conversion to liquid products (*46, 48*). Lurgi (*49*), and later Ruhrchemie (*47*), obtained more uniform temperature distribution by recycling 1 to 5 volumes of tail gas per volume of fresh gas, concomitantly attaining a higher olefin content in the product and significantly improving its quality.

2. Processes in which fixed beds of granular or pelleted catalysts are internally cooled by direct heat exchange; for example, hot-gas-recycle and oil-recycle processes.

In the hot-gas-recycle system, the heat of reaction is directly removed as sensible heat by the circulating gas. This process was developed in Germany by Michael (*6, 50*), who used a sintered-iron catalyst in a relatively simple converter without internal coolers in the reaction space. A longitudinal temperature gradient of about 10° C. was maintained along the bed by recycling 100 volumes of tail gas per volume of feed gas. The heat was recovered by generation of steam in an external heat exchanger. Despite the high gas flow, the control of temperature was difficult. An uneven pattern of gas flow over the cross section of the bed contributed to development of hot spots that caused excessive deposition of carbon and rapid deterioration of the catalyst. In addition, power requirements for circulating the large quantities of recycle gas were unavoidably high. Develop-

[a] Italicized figures in parentheses refer to items in the bibliography at the end of this report.

ment of this process never progressed beyond a large pilot plant.

Direct, internal heat removal is also accomplished in the oil-recycle process, which was first investigated by Duftschmid (*14*). The heat of reaction is absorbed as sensible heat and/or heat of vaporization by oil circulating through the submerged or wetted catalyst. Studies of this process have been made in the United States by the Standard Oil Development Co. (*35*), The Texas Company (*9, 40*), and the Federal Bureau of Mines (*8, 13*).

3. Processes in which finely divided catalysts are used in suspension, as in a liquid slurry or in the gas phase in a fluidized bed.

Synthesis in the slurry process is conducted by bubbling gas through a slurry or suspension of the catalyst in cooling oil. The heat of re-reaction is removed either by bayonet heat exchangers in the reaction zone or by circulation of the slurry through external heat exchangers. Early slurry experiments by German investigators at Rheinpreussen, Ruhrchemie, and I. G. Farbenindustrie were characterized by relatively short catalyst life, settling difficulties, and low space-time yields based on slurry and converter volume. However, in more recent experiments by Kölbel (*29*) of Rheinpreussen and by the Federal Bureau of Mines, high productivity, low gas yields, favorable product distribution, and long catalyst life have been achieved.

The dry-fluidized-bed technique, so successful in the field of catalytic cracking of petroleum, has been applied to the Fischer-Tropsch synthesis chiefly by Americans (*5, 23, 27, 30, 34, 37, 38, 39, 45*). Recently, some fluidized-bed studies have been conducted by Hall in England (*25*). In the fluidized system, fresh and recycled gas pass upward through a bed of fine catalyst particles suspended in the gas stream. The bed of solids behaves as a fluid, and the catalyst particles circulate to the cooling surfaces so that comparatively high heat-transfer rates are attained. Either fixed-fluidized or expanded-fluidized beds (dilute phase) may be employed. Most reactors have been of the fixed-fluidized type, with temperature control achieved either by bayonet heat exchangers in the top section of the reactor or, when small reactors are used, by jacketing the entire reaction zone. Although high space-time yields and favorable product distribution with high yields of gasoline are attained in this type of operation, the catalyst life is generally short, and yields of undesirable gas (C_1 plus C_2) may be high. Uniform fluidization is difficult to maintain in large-diameter reactors, and heat transfer may not be rapid enough.

When the gas-synthesis program of the Bureau of Mines was formulated late in 1943, virtually no published process data were available. A few details of the German dry-fixed-bed operations with cobalt catalysts were known, and the seemingly unavoidable disadvantages of low throughput and high steel requirements led to rejection of this operation. The hot-gas-recycle process was ruled out because of poor temperature control and high power requirements. Capable investigators in private industry in the United States were studying the dry-fluidized-bed process, and evaluation and development of this path of attack were left to them.

From the engineering point of view, processes employing the catalyst in direct contact with a cooling oil appeared as attractive as the dry-fluidized-bed approach and offered assurance of improved temperature control, easily constructed equipment, and comparatively low steel requirements. United States patents (1936–42) granted to the Standard Oil Development Co. and to the I. G. Farbenindustrie A.-G., although presenting only preliminary results and few data (*14, 15, 16, 17, 35*), supported the arguments that synthesis might be practicable in the presence of a liquid medium. Thus this type of process was selected for investigation by the Bureau of Mines. Initially, the oil-recycle process was studied; bench-scale studies of the slurry process were begun later.

This report on the development of the oil-recycle process covers:

1. Review of the work in Germany on the first oil-circulation process.
2. Work by the Bureau of Mines, United States Department of the Interior.

(*a*) Preliminary experiments on a laboratory scale, consisting of orientation tests and bench-scale operation employing a 1-foot bed of catalyst in a 3-inch-diameter vessel.

(*b*) Operation of 2 pilot plants with a 4- or 8-foot bed of catalyst in 3-inch diameter reactors. Up to 3 gallons of C_3+ hydrocarbons was produced per day in each of these plants.

(*c*) Operation of a barrel-per-day pilot plant with an 8-foot bed of catalyst in an 8-inch-diameter reactor.

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HISTORY OF THE OIL-RECYCLE PROCESS

WORK IN GERMANY

The first oil-recycle process for effecting the Fischer-Tropsch synthesis was developed by F. Duftschmid, E. Linckh, and F. Winkler (*14, 15, 16, 17*) of I. G. Farbenindustrie A.-G. during the period 1934–43. Results of this work first became available in the United States in 1947 through a report written by J. Foucher at the suggestion of Dr. W. F. Faragher, formerly chief of the Section of Synthetic Lubricants and Combustibles of Field Information Agency Technical (*50*).

After preliminary small-scale investigations, Duftschmid constructed a pilot plant with a reactor 0.2 meter in diameter, 6 meters in height and 200 liters (about 7 cu. ft.) in volume. Oil was circulated upward cocurrently with synthesis gas; as in all of Duftschmid's units, most of the heat of reaction was removed by vaporization of the oil. Initial operation, during 1936 and 1937, was conducted at high pressure (100 atmospheres); later work was done at medium pressure (15 to 20 atmospheres) in a two-stage operation. As might be expected, the oxygen content of the product increased with pressure. In general, the Germans did not consider use of high pressure (100 atmospheres) economical because of the increased costs for compressors and other equipment, even though the space-time yield of C_3+ hydrocarbons was increased from 600 to 3,800 kg. per day per $m.^3$ of catalyst.

A larger pilot plant with a 1,500-liter (about 50-cu. ft.) converter was put into operation in 1938. The reactor height was still 6 meters, but the diameter was enlarged to 0.5 meter.

Fused iron oxide (Fe_3O_4) was used in both pilot plants because of the need for a hard, durable catalyst. It was prepared similarly to the synthetic ammonia-type, fused-iron catalyst by melting metallic iron in a stream of oxygen and adding promoters. Common promoters were silicon, alkali, manganese, and titanium dioxide. The most frequently used catalyst (No. 997) had the following proportions:

	Grams
Iron powder	1,000
Silicon powder	25
Titanium dioxide	25
Potassium permanganate	50
Water	50

After fusion the cooled pig was crushed to ¼- to ½-inch particles that were reduced in a separate unit with dry hydrogen flowing at an hourly space velocity of 500 to 750. For the medium-pressure synthesis, reduction was conducted at 470° to 500° C. for 6 to 8 days; for high-pressure operation (100 to 200 atmospheres) reduction temperature was 650° C., but much less time was required. The reduced, cooled catalyst was stored under carbon dioxide until ready for use. A carbon monoxide-rich synthesis gas, $0.8H_2+1CO$, was used in most of the experiments. A series of tests at medium pressure showed a shift in product distribution toward lower boiling hydrocarbons, with increasing partial pressure of hydrogen:

Test No.	H_2:CO ratio			Percent of total product		Conversion of synthesis gas, percent
	Fresh feed	Usage ratio	Tail gas	C_3+C_4	>180° C.	
35	2.17	1.26	6.74	43	0	35.2
35-A	1.30	.90	3.20	41	12	33.5
35 B	1.34	.68	2.60	34	12	39.6
37	1.16	.72	1.55	32	22	37.8
31	.71	.72	.69	19	48	71.4

Although no mention of the C_1 plus C_2 yields was made, probably they also increased with increasing H_2:CO ratio in the feed gas. The conversion figures in the last column were not given in the original paper but are derived from the H_2:CO ratios. Because of the difference in conversion between the carbon monoxide-rich and hydrogen-rich gases, direct comparison of the specific yields may not be valid. Since Duftschmid stated that all of the tests were made under identical conditions, the relatively high conversion achieved with carbon monoxide-rich gas should make its use more economical than that of hydrogen-rich gas. A sulfur content of about 1.5 to 2 grains per 1,000 cu. ft. was the maximum found to be tolerable.

Most of the experiments were made at a minimum temperature of 230° to 240° C. at the bottom of the converter and with a fixed temperature differential of 50° C., so that the temperature at the converter exit was 280° to 290° C. Duftschmid predicted more efficient operation with a lower temperature differential, since he achieved only about one-fifth of the conversion in the lower half of the bed, but apparently the unit was never operated in such a manner. In most of his tests only 50-percent conversion was achieved in a single stage.