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 0.6 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	>190° C.	
35	3.17	1.28	8.74	43	9	35.2
35-A	1.90	.90	1.29	41	13	38.3
35-B	1.66	.92	2.62	35	13	29.8
37	1.15	.72	1.53	32	23	57.8
51	.71	.72	.62	10	46	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.

Because Duftschmid believed that greater productivity was obtained by evaporative cooling, a recycle oil containing components that evaporated under the operating conditions was used. A typical boiling range for recycle oil for synthesis at 25 atmospheres was:

Boiling range at 1 atmosphere, °C.:	Volume-percent
< 150	0
150–250	3
200–250	12
250–300	17
> 300	68

A specific yield of 145 to 150 grams of total product per cubic meter of converted gas was reported for a 2-stage operation at medium pressure, with an overall conversion of 75 percent—50 percent in each stage. Distribution and olefin content of the products were:

Product	Total product, weight-percent	Olefin content, percent
C_3+C_4	14	80
<100° C.	19	50–65
100°–150°	11	40–55
150°–175°	4	35–46
175°–320°	19	20–35
320°–430°	11	20
Total	78	

The remaining 22 percent of the product probably was C_1 plus C_2 hydrocarbons and oxygenated compounds. The primary gasoline had a research octane number of 68; the diesel oil a cetane number of 75 to 78.

When World War II started, further development of the oil-recycle process in Germany was curtailed. Although some improvements over the fixed-bed process had been achieved, notably in temperature control, efficient utilization of the synthesis gas had not been realized.

WORK OF THE FEDERAL BUREAU OF MINES

Until process development was started late in 1943, the Fischer-Tropsch research program by the Federal Bureau of Mines was concerned chiefly with developing and testing catalysts in narrow-tube, fixed-bed reactors, jacketed for heat removal. Before the oil-recycle process could be studied, the effect of cooling oil on the synthesis had to be determined; available information was rather meager. Consequently, in September 1943 tests were made to determine whether trickling a liquid hydrocarbon into the reactor during synthesis affected the activity of a pelleted, cobalt-thoria-magnesia-kieselguhr catalyst. Activities were measured during operation under the same conditions with and without the liquid. The temperature was controlled, not by the liquid but by the heat-exchange medium in the reactor jacket. The results indicated a slight loss of activity when the liquid was present.

A small, internally cooled unit was built in November 1943 for study of the synthesis at atmospheric pressure with the same cobalt catalyst. The reaction chamber consisted of an 18-inch length of 1.5-inch pipe filled with catalyst to a depth of 12 inches. The heat of reaction was to be dissipated largely by the latent heat of vaporization of the liquid. To observe the catalytic activity as a function of temperature during a trickle flow of oil, the reactor was kept adiabatic, with electric heat balancing the heat lost through the insulation. During December 1943 a test lasting approximately 150 hours was made with gas and oil flowing cocurrently downward at various rates at atmospheric pressure. Because the temperature was dependent upon the boiling range of the oil in this constant-pressure system, operating conditions were essentially fixed by the composition of the oil used. Erratic temperature control made a study of the catalyst activity impossible.

A larger reactor was constructed early in 1944. Again, heat was removed by evaporative cooling of oil, but greater range in temperature was attained by varying the operating pressure. Since the cross section of the reactor was about 4 times greater (3-inch standard pipe) than that of the smaller unit, the radial temperature gradient across the bed could be measured. Both cocurrent and countercurrent gas and oil flows through a 12-inch depth of pelleted cobalt catalyst were employed during 16 weeks of operation from May 1944 to April 1945. Good temperature regulation, with negligible radial or longitudinal gradients, was obtained with countercurrent flow at suitable pressures. The pressure required to attain a given temperature depended upon the boiling range of the cooling liquid. Satisfactory temperature control during cocurrent downflow operation was not achieved because the preheating zone for the gas-liquid mixture was not adequate. Consequently, the upper portion of the bed (entry) became overcooled; insufficient refluxing of liquid occurred, and excessive temperature variations resulted.

Enough evidence was obtained to show that neither the catalytic activity nor the distribution of products was appreciably altered by the presence of cooling liquid. Also, the trickling and refluxing of the liquid caused no erosion or attrition of the catalyst pellets. The practicability of temperature control of the synthesis by internal cooling seemed to be established, and larger scale experimentation appeared desirable.

Construction of the first pilot plant was completed in March 1945. The reactor was 3 inches in diameter and 8 feet in height. Improvements in the preheating sections were included in the unit, so that precise temperature control could be maintained with cocurrent down flow. Countercurrent tests were made, but because of high yields of gas and flooding difficulties at gas space velocities above 200, this mode of attack was abandoned after 2 experiments.

Several tests were made between April 1946 and May 1947 with cobalt catalysts and cocurrent downward gas-oil flow. Good temperature control was maintained along the 3-foot catalyst bed, except that a hot spot at the gas-and-liquid entry near the top of the bed was especially troublesome at space velocities above 300. To eliminate this difficulty the oil was returned from the overhead condenser to the top of the reactor by means of a pump rather than by gravity flow; thus more or less uniform distribution was forcibly effected over the cross section. With this arrangement a space velocity of 450 was found to be the maximum rate tolerable in single-pass operation. The space-time yield of C_3+ hydrocarbons was about 600 kg. per m.^{3} of catalyst volume per day. At higher throughputs complete elimination of the hot spot was not achieved.

The final experiment with cobalt was made in April 1947, with the bed completely submerged in the cooling medium rather than just wetted. Upward cocurrent flow was employed with the gas and liquid fed into the bottom of the reactor. About the same catalyst activity was obtained with this type of operation as had been observed with the wetted catalyst bed.

As enough information on the performance of cobalt in the presence of a liquid medium had now been obtained, investigation of this material was discontinued; and cheaper and more abundant iron catalysts were then investigated. Higher productivity and more favorable product distributions were reported. From June to September 1947 experiments were made with pelleted and granular, precipitated-iron catalysts and $1H_2+1CO$ feed gas. Both the trickle-flow, wetted bed and the completely submerged bed were used. Heat was removed mostly by vaporization of the oil. Although activities and temperature control were satisfactory, each of these tests lasted only a few weeks because of excessive pressure drops resulting from disintegration and agglomeration of the catalyst.

Fused, synthetic ammonia-type catalysts were next used in the synthesis because they are hard and have high resistance to crushing. All tests with these catalysts were made in submerged beds. The smoothest operation was achieved when the heat was removed, primarily as sensible heat by a circulating oil stream. Synthesis gas and recycle oil were fed cocurrently into the bottom of the reactor; they flowed upward and left through an overflow pipe installed about 2 feet above the catalyst level. An extremely important advantage of this method over evaporative cooling became evident at once, namely, that pressure and temperature were thus made essentially independent of each other, and operation became more flexible.

Several experiments were made at 300 pounds per square inch gage (p. s. i. g.) pressure and at hourly space velocities of 100 to 300, with $1H_2+1CO$ feed gas, both with and without gas recycling. A progressively increasing pressure drop along the bed interfered with the flow of recycle oil and necessitated shutdowns after 1 to 3 months of operation. When the converter was opened, the catalyst particles were found to have retained their original size. However, they had been cemented together tightly and could be removed only by drilling. Subsequent attempts to prevent this effect in the fixed-bed failed, although the rate of cementation was retarded considerably when a hydrogen-rich gas was used.

Cementation was eliminated in April 1949 by the use of an expanded bed of catalyst. In the expanded-bed system, smaller catalyst particles and higher linear velocities of oil were used than in the fixed bed. The rate of upward flow of recycle oil through the catalyst was adjusted so that the bed was expanded about 25 to 35 percent. Hence, the particles were kept in motion but confined within the reactor. Expanded-bed operations with synthetic-ammonia catalysis were conducted several months without notable increase in pressure drop or evidence of cementation. With synthesis gas compositions $1H_2+1CO$, $1.3H_2+1CO$, and $2H_2+1CO$, loss of catalyst by carryover from the converter to the oil-circulating lines was negligible, even after 4 months of operation, although sieve analyses showed that some attrition of the catalyst had taken place. With a carbon monoxide-rich gas ($0.7H_2+1CO$), however, severe catalyst losses occurred after a few months in several experiments, indicating that chemical environment as well as mechanical erosion influenced the rate of catalyst decomposition. Even with this gas, operation for more than 1,500 hours was possible when the carbon dioxide was removed from the gas that was recycled to the converter. Expanded-bed operations in two 3-inch reactors during the period from May

1949 to March 1951 are reported. Space velocities of 300 to 1,000, pressures of 300 and 400 p. s. i. g., gas compositions varying from $0.7H_2+1CO$ to $2H_2+1CO$, and gas conversions of 70 to 90 percent were investigated.

A 1-barrel-per-day pilot plant with an 8-inch-diameter reactor was placed in operation in May 1951. The reactor originally was designed to accommodate a 16-foot height of catalyst for fixed-bed operation. Because the space-time yield of C_3+ hydrocarbons had been considerably increased by using an expanded bed, only an 8-foot height of catalyst was required for the barrel-per-day production. It was not possible to employ a deeper bed of catalyst because the supply of synthesis gas was limited. Two runs were made in this unit, and the temperature control along the bed was quite satisfactory, as it had been in the small units. No difficulties were encountered in mechanical operation of the plant; however, the catalyst was less active and stable than at comparable conditions in the small pilot plants.

A range of typical operating conditions and yields for each stage of development is given in table 1. Data are included also for tests made in small dry-bed reactors with cobalt and precipitated iron catalysts. These small testing units are particularly valuable for assaying catalysts to measure relative catalyst activity. A comparative evaluation of the character and distribution of the products from these dry-bed units is valuable. However, temperature control under adiabatic conditions in the catalyst testing reactor cannot be studied, as the reaction tube (0.625 inch inside diameter) is surrounded by a bath of boiling Dowtherm to maintain a constant temperature. Process-development and operability studies were the principal goals of the pilot-plant tests. Adequate removal and transfer of heat, and physical problems related to catalysts, such as agglomeration, carbon deposition, and disintegration, had to be investigated on a pilot-plant scale. A more characteristic study of the products was made by operation of the pilot plant.

From the data in table 1 some idea can be obtained of the changes in operation and results that occurred during the various phases of the investigation. A range of temperatures and yields is shown for each operation to summarize the conditions that were explored. As discussed later (see Experimental Work, p. 8), the yield and distribution of products are affected by many variables such as the temperature and pressure of the catalyst, H_2:CO ratio of the feed gas, and possibly the space velocity of the gas. Data are given for expanded-bed experiments of several feed gas ratios because change in the H_2:CO ratio affected the durability of the catalyst, as well as the products. Similar product yields and distribution were obtained in the 3-inch- and 8-inch-diameter reactors for the same feed gas.

TABLE 1.—*Comparison of typical operating conditions and yields with cobalt and iron Fischer-Tropsch catalysts*

Main catalyst constituent	Cobalt			Iron									
Preparation of catalyst	Precipitated					Fused							
Activation with	H_2 reduction and synthesis-gas induction			Synthesis gas		H_2 reduction and synthesis-gas induction							
Synthesis: Mode of operation	Dry bed[1]	Co-current	Countercurrent	Dry bed[1]	Co-current	Fixed bed		Expanded bed					
								3-inch-diameter reactor				8-inch-diameter reactor	
Average temperature, °C.	180-190	185-210	165-190	230	235-250	250-265	245-265	240-270	240-270	240-250	250-270	250-265	250-265
Pressure, p. s. i. g.	150	85-170	60-90	100	50-150	300	300	300-400	300-450	300	300	400	400
Space velocity, hr^{-1}	100	100-600	100	100	100	300	300	300	600-1,000	600	600	450	600
H_2:CO, fresh gas	2.0	1.5-2.1	2.1-2.2	1.3	0.9-1.0	1.0	1.5	0.7	1.0	1.3	2.0	0.7	1.0
Gas-recycle ratio	None	None	None	None	None	2.0	1.0	1.0	1.0	1.0	1.0	1.0	1.25
Conversion of synthesis gas, percent	70-75	32-75	41-78	70	60	70	70	70-80	70-90	75	70	70	70
Maximum catalyst life, hr.	(3)	(3)	(3)	(3)	(3)	2,100	2,200	1,500	2,500	2,650	(3)	(3)	(3)
Yields:													
C_1+C_2, gm. per m.³ H_2+CO converted	15-45	30-62	66-75	65	20-30	85	35-40	20-30	30-35	30-35	45-50	20-25	25-30
C_3+ ...do	100-150	120-175	134-150	190	170-180	160-175	160-185	165-175	160-175	160-175	140-170	180-190	160-170
Space-time yield of C_3+, kg. per m.³ cat. vol. per day	100-250	240-450	170-330	300	240	400	750	1,650-2,200	1,600-2,000	1,600	1,400	1,600	1,600
Product distribution, wt.-percent of C_3+:													
Gasoline (C_3—204° C.)	35-40	40-45	(3)	55-65	(3)	65-80	60-65	40-55	50-60	50-65	(3)	40-50	60-65
Diesel (204°-316° C.)	35-30	20-25		10-20		10-20	10-15	10-15	10-15	10-20		15-20	10-15
Heavy distillate (316°-450° C.)	10-20	10-20		15-20		10-15	10-15	15-25	15-20	10-15		15-20	10-15
Wax (>450° C.)	15-25	15-20		10-20		10-15	10-15	10-25	10-15	10-15		20-25	10-15

[1] See ref. [illegible] in Bibliography. [2] See ref. [illegible] in Bibliography. [3] Not determined.