EXPERIMENTAL WORK

BENCH-SCALE, TRICKLE-FLOW INVESTIGATIONS

OBJECTIVE

Preliminary tests in 1943 and 1944 indicated the feasibility of dissipating the exothermic heat of the Fischer-Tropsch synthesis from the reactor by internal evaporative cooling with a liquid hydrocarbon; however, adequate temperature control was not obtained in these early experiments. Erratic temperatures in the crude laboratory unit first employed were believed to have resulted largely from uneven distribution of the cooling liquid that trickled directly onto the catalyst by gravity from a reservoir above the converter. The early experiments had also been confined to operation at atmospheric pressure with the synthesis temperature automatically limited by the boiling range of the cooling liquid.

To increase the flexibility of the process, a bench-scale unit with a pressure-regulating system was constructed in 1944 so that the boiling range of the coolant in the reactor and consequently the operating temperature could be varied at will. The catalyst bed was 3 inches in diameter and 1 foot in depth, dimensions that were considered adequate to reduce substantially the wall effects and allow a study to be made of the temperature gradients and the activity of the wetted catalyst.

The goal of this part of the program in developing the gas-synthesis process was to meet or surpass the catalyst longevity and productivity that had been attained in the narrow-tube, fixed-dry-bed reactors by the Federal Bureau of Mines. Acceptable performance by this standard would mean a minimum catalyst life of 3 months, 60- to 70-percent conversion of feed gas in single-pass operation, and a $C_1 + C_2$ fraction not exceeding 20 weight-percent of the hydrocarbon product.

APPARATUS

One of the more important advantages of an internally cooled converter is simplicity of design. Figure 1 shows the bench-scale reactor referred to above. This reactor consisted of a 24-inch length of 3-inch Schedule 40 iron pipe with 7 radially placed, ¼-inch thermocouple wells of standard pipe in the catalyst zone about 2 inches apart. Another thermowell coaxial with the reactor made temperature readings possible at any point along the vertical axis in or above the 12-inch bed of catalyst. The upper 12 inches of the reactor was filled with 4- to 6-mesh Aloxite granules. This section served both as a distributor and as a preheating zone for the cooling liquid that trickled in from the liquid makeup tank or refluxed from the partial condenser installed directly above the packed section. This electrically heated condenser contained boiling water in the jacket; the temperature was controlled by the pressure of nitrogen above the boiling liq-

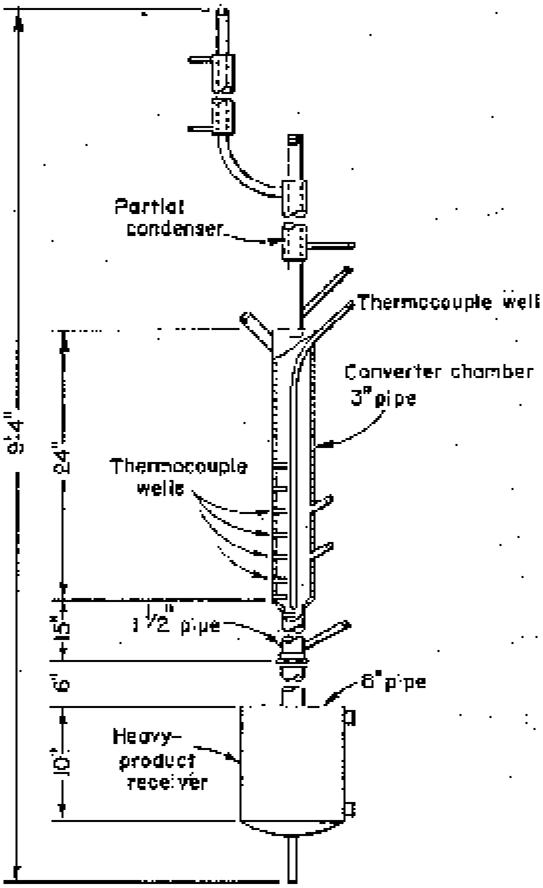

FIGURE 1.—Bench-Scale, Internally Cooled Converter.

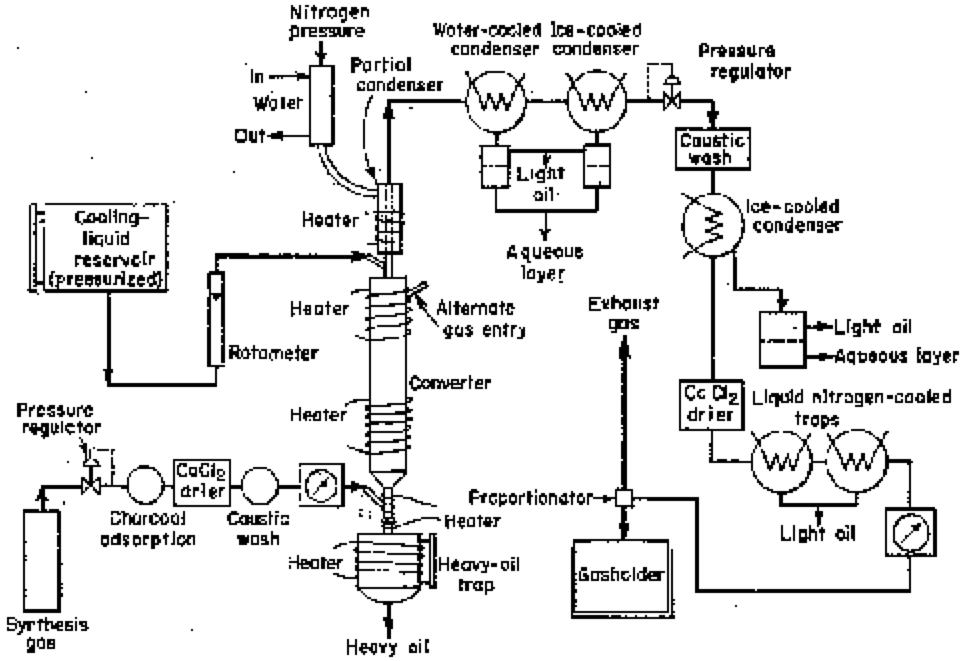

FIGURE 2.—Bench-Scale, Internally Cooled Converter System.

uid. The constant-temperature bath thus effectively controlled the temperature and vapor content of the exit gases. Below the converter tube a 15-inch length of standard 1.5 inch pipe, also filled with 4- to 6-mesh Aloxite, served as a preheating and saturation zone for the feed gas. About 6 inches below the gas entry was an electrically heated receiver into which the heavy products and excess cooling oil drained. The receiver was kept at system pressure.

Figure 2 is a flow diagram of the system, designed either for countercurrent or cocurrent flow; the cooling liquid flowed downward in either case. When the system was operating countercurrently, synthesis gas entered the packed, preheating zone near the bottom of the reactor and flowed upward through the reaction zone. Most of the coolant vapor and some of the product, which were carried out of the reaction zone by the gas stream, condensed in the partial condenser and returned to the catalyst as liquid. The amount of fresh liquid added to the reactor during operation was therefore only a small fraction of the amount that, on a once-through basis, would be vaporized by the heat of reaction. This small quantity of liquid was needed primarily to replace entrained oil and to minimize the probability of dry spots developing within the reaction zone. The higher boiling hydrocarbon products, with the excess coolant, flowed downward into the heavy-oil trap, which was discharged periodically. The overhead vapors and permanent gases leaving the partial condenser flowed to water- and ice-cooled traps maintained at system pressure. Most of the water formed in the synthesis was recovered here. Just beyond these traps the pressure of the gas was reduced to atmospheric by a back-pressure regulator. From the downstream side of the regulator the gas flowed through a carbon dioxide scrubber, an ice-cooled trap, and a drying tube and finally to liquid-nitrogen-cooled traps. The gas was metered, and a proportioned sample was removed for analysis; the remainder was discharged to the atmosphere.

During cocurrent-flow experiments, the gas entered the converter through a port just above the Aloxite packing and flowed downward through the reaction zone. The gas left the bottom of the reactor just above the heavy-oil trap, flowed to the water-cooled trap, and then followed the path previously described.

RAW MATERIALS

SYNTHESIS GAS

Synthesis gas was produced by the reaction of natural gas with steam and carbon dioxide by the conventional catalytic hydrocarbon-reforming process. H_2:CO ratios were varied from 10 to 0.25. The hydrogen and carbon monoxide content of the synthesis gas usually exceeded 99 percent; methane, carbon dioxide, and nitrogen were present as fractions of 1 percent each. The sulfur content was maintained at less than 0.1 grain per 100 cu. ft. of gas.

CATALYST

Cobalt was chosen as the type of catalyst to be initially studied in the oil-recycle process for two reasons. First, a considerable background of fundamental data had been obtained in the narrow-tube, dry-bed test units. Second, it was desired to determine whether use of cobalt in an oil-circulation process would increase the space-time yield of C_3+ material and the olefinic content of these hydrocarbons, as compared with data reported for German commercial plants with dry beds operated at medium pressure.

The catalyst employed for this series, and identified as the Hall catalyst, was promoted cobalt carried on a support. It was prepared by precipitation and subsequently formed into ⅛- by ⅛ inch cylinders in a pellet press. The composition, in terms of weight units, corresponded to this proportion:

$Co:ThO_2:MgO$:kieselguhr::100:7:12:200 (*7*, *43*).

COOLING OIL

The coolant fluid was obtained from a commercial grade of naphtha by fractional distillation. To avoid the potential hazard of poisoning the catalyst, the cut selected for use was desulfurized by a vapor-phase hydrogenation over a cobalt-molybdate catalyst.

OPERATION

The catalyst pellets were reduced at 400° C. in the converter with dry hydrogen for 2 hours at atmospheric pressure; the hydrogen flowed at rates corresponding to hourly space velocities varying between 1,500 and 6,000. At the end of the reduction period the temperature was lowered to 160° C., the flow of hydrogen was reduced to a nominal rate, and induction was begun. In all of the experiments of this series, the induction method that was employed followed closely the procedure developed by the British Fuels Research group (*22*): With hydrogen flowing at about 5 cu. ft. per hr. (an hourly space velocity of 100), pressure at 60 p. s. i. g., and temperature at 160° C. a small flow of cooling oil was passed over the catalyst for 1 hour (2 to 3 liters of oil) to insure saturation of the bed with liquid. At the end of this period the pressure was reduced to atmospheric, and the temperature fell simultaneously as liquid flashed away on reduction of pressure. At this point the flow of hydrogen was discontinued, and a small flow of $2H_2-1CO$ synthesis gas was introduced. System pressure was again quickly built up to 60 p. s. i. g., the flow of cooling liquid was set properly (500 and 2,000 ml. per hr., respectively, for countercurrent and cocurrent operations), and the flow of synthesis gas was adjusted to an hourly space velocity of approximately 100. Temperature was rather quickly increased to 150° C. and maintained for 2 hours; then, by periodic adjustment of the pressure, the temperature was increased to 175° C. at a reasonably uniform rate over the next 4 hours. The input of cooling liquid was reduced, usually, to between 200 and 400 ml. per hr. before the end of this period, to operate at the lowest practicable rate of flow required to control the reaction and yet provide a small excess to insure uniform wetting. When the 175° C. temperature had been reached, induction was considered complete, and operation was continued indefinitely at this temperature until a change in catalytic activity necessitated temperature adjustment. A temperature increase was affected by increasing the pressure on this system, and, conversely the temperature was lowered by pressure reduction. Liquid products were discharged periodically through manually controlled valves.

RESULTS AND DISCUSSION

A series of 4 trickle-flow experiments (FT-85 to FT-88), with a total operating time of 16 weeks, was sufficient to furnish all process data needed at this scale of operation to plan for the next step of expansion of the oil-recycle process. Table 2 presents summary data from this series for selected periods of good catalyst performance. No data from experiment FT-86 are reported because the activity of the catalyst was poor.

Throughout this series the pressures, gas-throughput velocities, and reaction temperatures were maintained, in general, near the values found to be optimum in the fixed-dry-bed reactors in current use. Thus, the only experimental variables subject to study were composition and rate of flow of the coolant fluid. These were varied to establish the conditions at which best performance was reproducibly obtained.

The degree of success attained is found by comparing the values for contractions and specific yields of C_1 plus C_2 hydrocarbons in table 2 with the following values representative of good productivity in a fixed-dry-bed experiment:

Synthesis gas	S. V. H.	100
Contraction	vol.-percent	74
Pressure	p. s. i. g.	100
Temperature	°C.	190
Yields, specific, gm./m.^{3}:		
C_1-C_2		33.4
C_3+		131.1

TABLE 2.—*Bench-scale, trickle-flow experiments with cobalt*

Experiment No.	FT-85c	FT-87b	FT-88a	FT-88b	FT-88c	FT-88d
Duration, hr	91.8	81.1	88.3	77.2	101.9	114.5
Catalyst:						
Total age, hr	483	486	332	382	362	352
Volume, cu. ft.	0.053					
Mode of operation	Countercurrent			Cocurrent		Countercurrent
Oil:						
Boiling range at 1 atm., ° C.	130–150	110–140	110–125	110–125	110–125	110–125
Flow, ml. per hr.	260	260	400	2,110	1,910	800
Synthesis gas:						
Ratio in fresh gas, H_2:CO	1.67	1.94	2.13	2.08	2.08	2.13
S. V. H.[1] (settled bed)	99	64	121	122	100	104
Flow, cu. ft. per hr. (S. T. P.)	5.50	3.38	6.51	6.57	5.38	5.60
Contraction, vol.-percent[2]	60.1	48.5	48.4	50.2	45.9	54.3
Conversion, vol.-percent H_2+CO	61.5	49.8	48.8	50.7	46.4	54.8
Usage ratio, H_2:CO	1.87	2.17	2.21	2.07	2.00	2.14
Pressure, average, p. s. i. g.	87.2	66.7	68.9	71.4	67.5	84.0
Ave. temperature, ° C.	193	184	173	175	178	189
Yields, specific, gm. per m.³ C_1+C_2	46.7	83.9	51.9	30.0	46.3	57.4

[1] See Glossary (p. 70).

[2] Measured after passage through liquid-nitrogen traps so that gas was virtually free of hydrocarbons.

Comparison shows that neither countercurrent nor cocurrent trickle-flow operation afforded conversion as high, or gaseous hydrocarbon production as low, as fixed-dry-bed operations.

The comparatively close approach of the usage ratio to a value of 2.0, ideal for the synthesis reaction catalyzed by cobalt, is a good indication of favorable product distribution, that is, preponderance of liquids and solids. High yields of methane would have resulted in a usage ratio closer to 3.0. No direct measurements of liquids and solids production were undertaken for this series, because early in the work it became evident that the procedures for separating coolant from product would be too laborious and complex to be justified at this scale of operation.

The data in table 2 indicate a slight but positive advantage, with respect to controlling the production of low-molecular-weight hydrocarbons, when gas flow was cocurrent with the liquid. When operated in this manner the liquid coolant input was about 10 times the quantity required in countercurrent operation, since there was virtually no liquid reflux.

In general, process performance obtained in this series of experiments met expectations rather well. Under countercurrent flow conditions, operation was continuous and trouble free. Radial temperature gradients were negligible, and longitudinal gradients did not exceed 5° C. Cocurrent operation was usually difficult to control; slight variations in either coolant or gas flow initiated wide fluctuations in temperature, and consequently fluctuations in gas conversion.

Catalyst life was apparently not adversely affected, either chemically or physically, by the comparatively severe treatment inherent to the process. When discharged, the pellets were found to be intact.

PILOT PLANTS[7]

THREE-INCH-DIAMETER REACTOR

OBJECTIVE

To investigate the principle of direct internal cooling on a larger scale and make a fairly complete process study, a pilot plant with a 3-inch-diameter reactor and an allowable bed depth of 8 feet was built. It was completed in March 1946. It was designed for operation with countercurrent or cocurrent flow. The 8-foot bed would permit a more complete, accurate study of the longitudinal temperature gradients than the 1-foot bed that had been used previously.

The program followed in the pilot plants can be divided into three parts that are separately reviewed in the remaining portion of this report.

1. Trickle-flow experiments. This group comprises experiments 1 to 5–E, employing pelleted cobalt catalyst, and experiments 7 to 9–B, employing precipitated iron.
2. Submerged fixed-bed experiments.
   (a) Preliminary tests, comprising 2 tests made with pelleted cobalt (experiments 5–F and 6) and 1 with

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[7] The pilot plants were operated by A. J. Forney, R. M. Jimeson, T. E. Ross, W. P. Haynes, J. S. Tosh, G. E. Johnson, M. Fenton, D. Chiswell, F. J. Schwaneweg, L. Chottiner, and D. Bornstein. Construction of the units was supervised by W. H. Williams.

Chemical analyses were performed by the staff of the Analytical Chemistry Section of the Synthetic Fuels Research Branch under the supervision of H. D. Finkel, M. E. Kunder, and W. E. Dieter. X-ray and magnetic analyses of the catalysts were conducted by L. J. E. Hofer, W. C. Peebles, and E. M. Cohn; and mass spectrometric and infrared analyses were made by R. A. Friedel, A. G. Sharkey, and J. L. Shultz.