EXPANDED-BED EXPERIMENTS

INTRODUCTION

To eliminate agglomeration of the catalyst, a different method of operation, "expanded catalyst bed," was instituted, beginning with experiment 18. The general principles of this system have been described by Atwell (4). An important feature of this mode of operation is that the linear velocity of the cooling oil is increased to such a value that the catalyst bed (8- to 42-mesh particles) expands until its height is 5 to 30 percent greater than its settled volume. A comparatively high degree of agitation is thus imparted to the individual particles, especially when the bed is expanded 30 percent.

Before this system was used in actual synthesis, a series of experiments was conducted in a glass column at atmospheric pressure and room temperature to determine the liquid-gas ratios and flow rates required for a given bed expansion while at the same time avoiding flow rates that would carry catalyst out of the converter. For this study a mixture of about 10 volume-percent carbon dioxide and 90 percent nitrogen was substituted for synthesis gas, and a light cut of Barnes oil was employed as the liquid medium. The physical properties of this oil under these conditions were similar to those of the cooling oil under synthesis conditions. The data were extrapolated to synthesis conditions on the basis of equivalent linear velocities of gas and liquid. For hourly space velocities of fresh gas between 600 and 900 and for recycling ratios of 1 to 2, an oil flow of 0.10 to 0.30 ft. per sec. produced a satisfactory bed expansion.

In the expanded-bed series of experiments (Nos. 18 to 31) a synthetic-ammonia-type iron catalyst was kept on stream as long as 4 months with no cementation and consequently without any increase in the pressure drop through the bed. Other advantages of the expanded bed over the fixed bed were:

1. *Greater catalyst economy.*—Use of smaller particles resulted in greater total production per pound of catalyst.
2. *Lower operating temperatures.*
3. *Easier charging and withdrawal of catalyst.*
4. *Lower consumption of mechanical energy;* that is, the pressure drop across the moving bed was almost independent of the rate of oil circulation within the range of flow employed.
5. *Greater space-time yield,* based on converter volume as well as catalyst volume.

APPARATUS

The equipment was basically the same as that used in the fixed-bed experiments, but a few modifications and additions were made.

To prevent wax from entering the overhead condenser and obstructing the reflux line, as

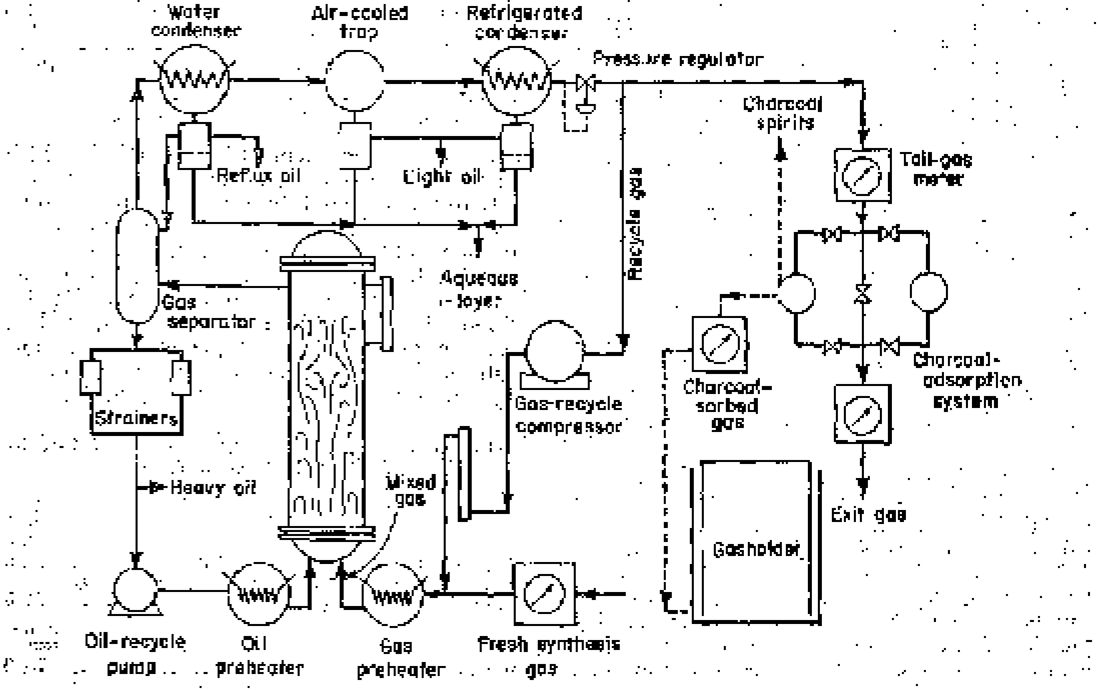

Figure 9.—Submerged, Expanded-Bed Process.

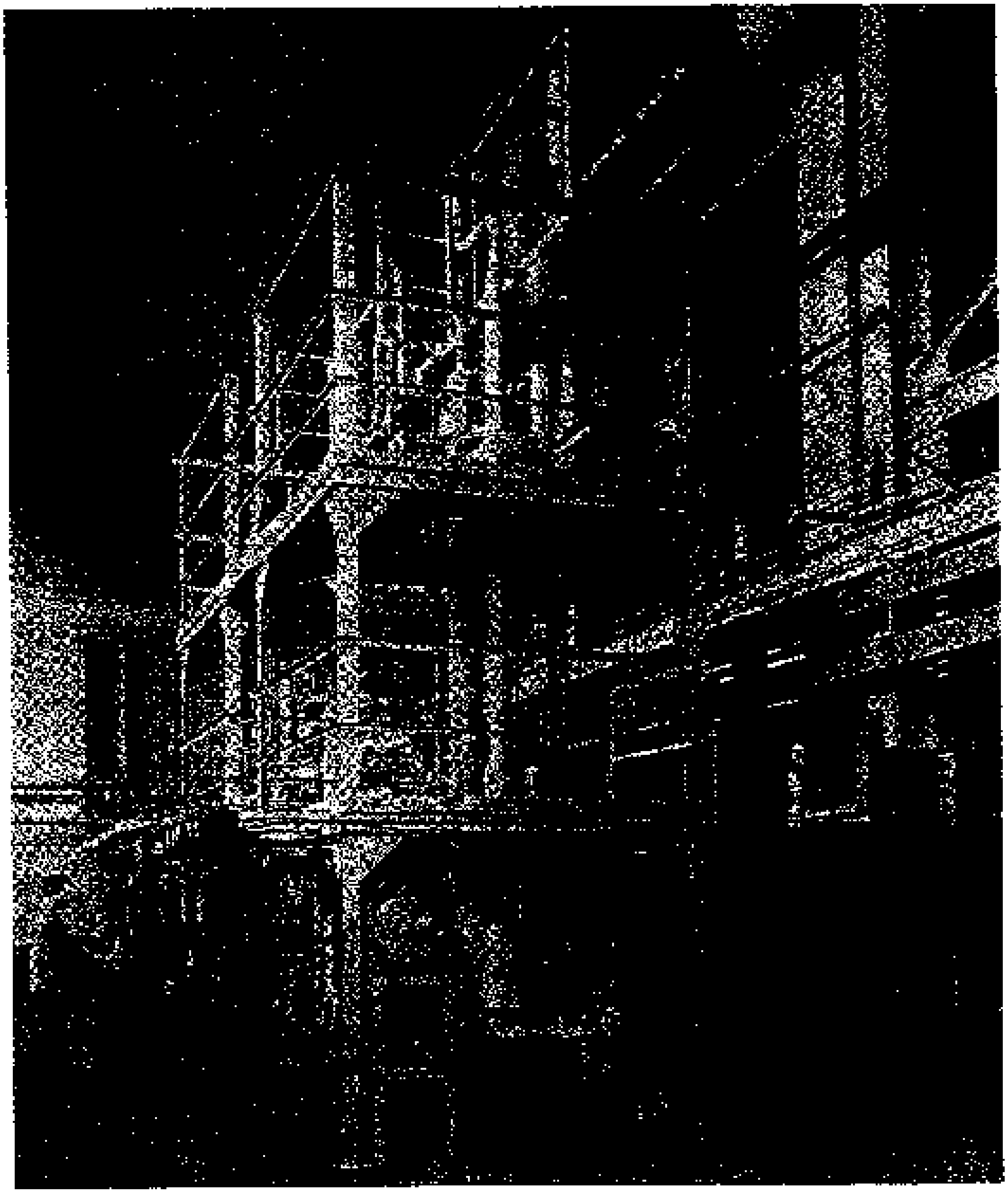

FIGURE 10.—Pilot Plants 1 and 2 for Internally Cooled, Gas-Synthesis Process.

had occurred during experiment 17, a 6-inch-diameter, 2-foot-long separator was installed in both units in the side arm where the oil first left the converter (fig. 9). Better separation of gas and entrained liquid was thus achieved, and carryover of wax was avoided. In addition, the gas separator served as a small reservoir for the cooling oil and eliminated severe fluctuations in the liquid level when the rates of flow of gas or liquid were changed. A photograph of the pilot plants is shown in figure 10.

After experiment 18, which served as an orientation run, a ball float was installed in each of the converters to indicate the height of the catalyst during operation. The specific gravity of the float caused it to sink in the clear oil but float on top of the moving catalyst. A light rod attached to the top of the ball extended through the upper portion of the converter into a sight glass. The rate of oil circulation was easily adjusted so that the top of the extension rod was maintained at the proper height.

Before experiment 22 was begun, unit 2 was modified so that it could be operated at pressures up to 500 p. s. i. g. Alterations were concerned for the most part with changing the reactor system and its associated piping to conform to Schedule 80 piping. In addition, a larger oil-circulation pump, a bauxite reactor, and a scrubbing system for removing carbon dioxide were installed as parts of the synthesis plant (fig. 11).

The bauxite reactor, a 2-foot length of pipe 4 inches in diameter charged with about 0.133 cu. ft. of catalyst, was installed in the overhead line between the converter and the reflux condenser. The unit was heated electrically, and close temperature control was maintained. All overhead gases and oil and steam from the gas separator passed through the bauxite catalyst, where most oxygenated compounds were decomposed to olefins. The light hydrocarbons, including those formed in the bauxite reactor that were not recovered in the water-cooled condenser, air-cooled trap, or refrigerated condenser were returned to the converter with the recycle gas. A bypass allowed comparative data to be obtained with and without the bauxite reactor in service.

The scrubber, placed in the gas-recycle line after the refrigerated condenser, removed carbon dioxide from the gas before it was returned to the converter. Water was the first scrubbing agent that was used (fig. 12). Tail gas from the recovery system entered the 6-inch-diameter scrubber at converter pressure countercurrent to a stream of circulating water that was injected through spray-type nozzles at the top of the column. The column was packed with ½-inch Raschig rings to a height of 69 inches. The scrubbed gas was then recycled from the top of the scrubbing unit to the converter. The amount of carbon dioxide remaining in the gas was continuously recorded by a gas analyzer in the line. The effluent water, containing dissolved gases (mainly carbon dioxide) at operating pressure, passed into a tank in which a constant liquid level was maintained. From there it flowed into a 6-inch-diameter stripper column filled with ½-inch Raschig rings to a height of approximately 32 inches, where the pressure was reduced to about atmospheric. In this manner the major portion of the dissolved gases was released from solution in the water and purged from the system. Water was returned under pressure to the top of the scrubber.

After a short period of operation loss of synthesis gas due to its solution in water was found to be excessive, and the scrubbing system was modified as shown in figure 13. Water was replaced by a 15-percent (by weight) solution of potassium carbonate. The overall system was basically the same, except that the spent solution entering the stripper column had to be heated to decompose the bicarbonate and regenerate the carbonate. The solution was heated to about 90° to 95° C. in a coil jacketed by low-pressure steam (10 to 12 p. s. i. g.). The reservoir was also steam-jacketed to maintain the temperature of the solution. More surface was necessary for regeneration, so the length of the stripper column was increased, and 2 more feet of packing was inserted. The hot, regenerated solution of potassium carbonate flowed from the bottom of the reservoir to a cooler, where it was cooled to about 30° C. From the cooler it was returned under pressure to the top of the scrubbing unit. Eventually the carbonate solution was replaced by a 20-percent (by weight) solution of monoethanolamine that was much more effective.

Unit 1 was used also in special tests (experiment 23) in conjunction with a 6-inch-diameter stripping column packed with ½-inch Raschig rings to a height of 6 feet. Operation with this unit is discussed later.

RAW MATERIALS

SYNTHESIS GAS

Synthesis gas was produced as reported under Bench-Scale, Trickle-Flow Investigations (p. 9).

CATALYST

For the initial expanded-bed tests, experiments 18 to 20, fused iron (catalyst D-3000.1) was used again. Beginning with experiment 21 catalyst D-3001 was used; more of it was available, and activity tests had shown little

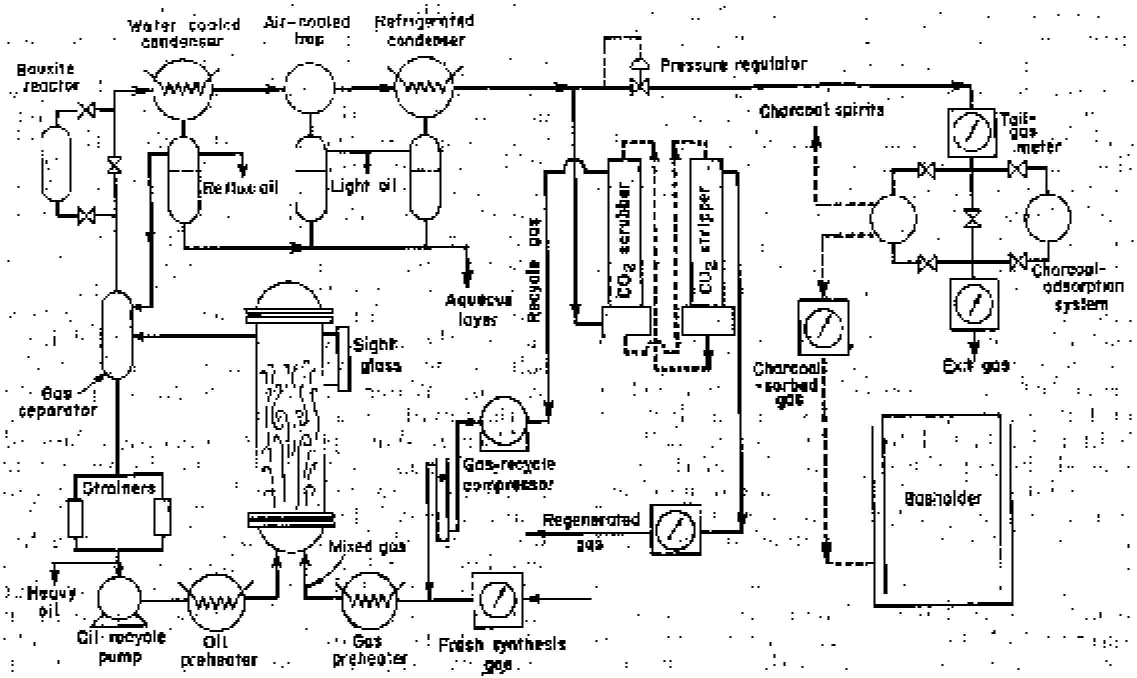

FIGURE 11. Submerged, Expanded-Bed Process, Showing Bauxite Reactor and Carbon Dioxide-Scrubbing System.

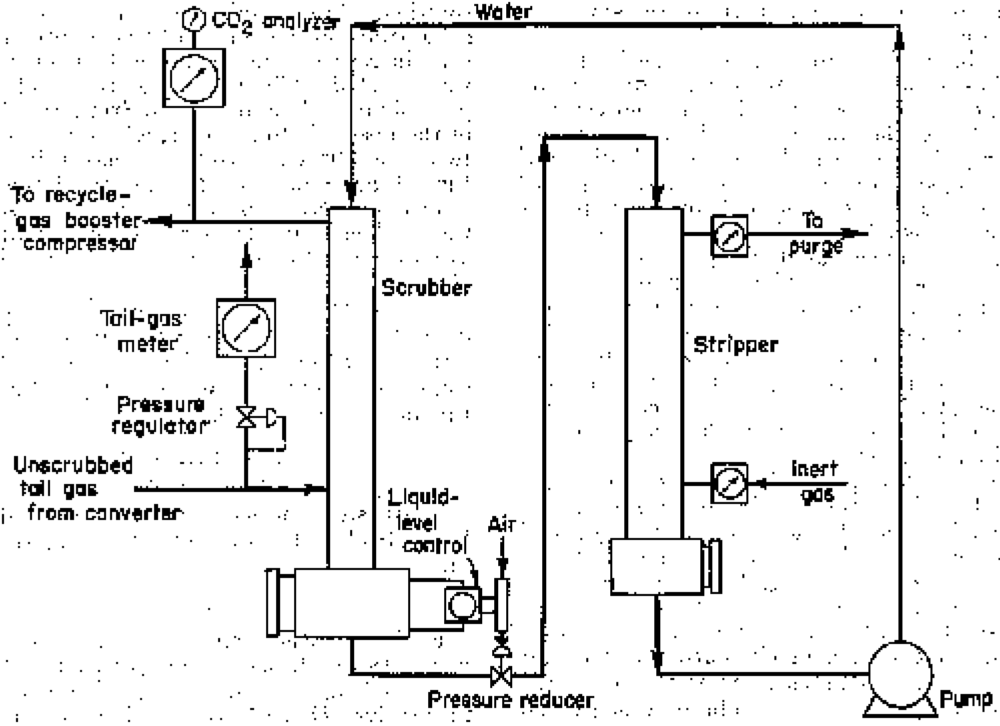

FIGURE 12.—Carbon Dioxide-Scrubbing System, With Water Used as Scrubbing Agent.

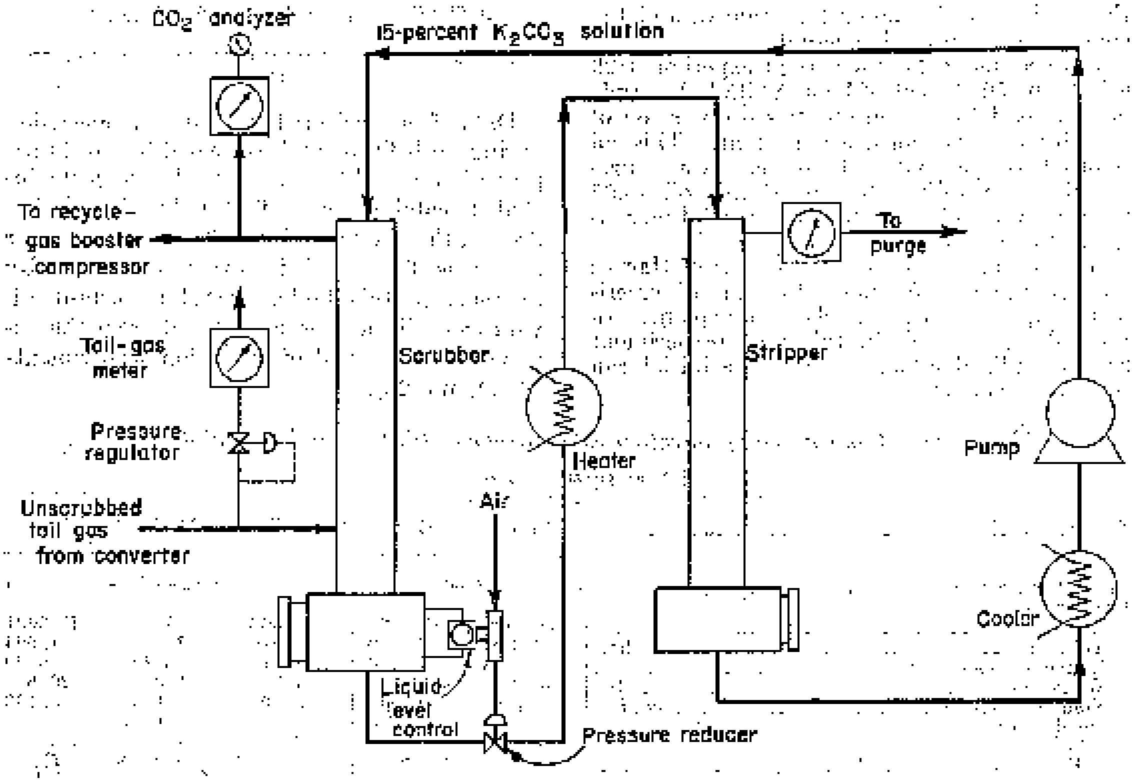

FIGURE 13.—Carbon Dioxide-Scrubbing System, With 15-Percent Potassium Carbonate Solution Used as Scrubbing Agent.

difference between the two catalysts. Two similar fused catalysts, prepared at the Federal Bureau of Mines Demonstration Plant in Louisiana, Mo., were tested later (experiments 28 to 29).

The range of mesh sizes was 8 to 16 in experiment 19; 20 to 42 in experiments 20 and 21; and 6 to 20 in the other tests. Because the geometric surface of the 20- to 42-mesh particles was about 2.8 times greater than that of the 6- to 20-mesh particles, much greater activity was expected. However, under comparable operating conditions, the activity allowed a decrease in temperature of only 5° to 10° C. Moreover, attrition and carryover made the small particles unsuitable for the expanded-bed system.

As in the fixed-bed experiments, catalysts were reduced with hydrogen to metallic iron before induction and synthesis. Beginning with experiment 21, the method of reduction was modified. Work in laboratory-scale units had shown that increasing the hydrogen flow rate from 2,000 to 8,000 in terms of hourly space velocity had produced a more stable and somewhat more active catalyst. One explanation of this finding would be that, at the higher rates of flow, the concentration of water vapor was appreciably lowered and that water vapor was evolved at a more uniform rate during reduction. To achieve a similar effect at an hourly space velocity of 2,000 in the pilot-plant reduction unit, the temperature of the reaction zone was increased at a controlled rate so that the concentration of water vapor in the exit gas never exceeded 8.0 gm. per $m.^3$, the saturation concentration at 5° C., in the gas cooler. The temperature was raised rapidly from room temperature to about 300° C., then increased only about 5° C. per hour until 500° C. was reached. Reduction was continued at this temperature until the concentration of water vapor in the exit gas approached that of the inlet gas (less than 0.8 gm. per $m.^3$). The time required for reduction was thus extended from 48–72 to 90–150 hours. The advantage of this method was never demonstrated clearly in the plant.

COOLING OIL

A 300° to 450° C. cut of oil produced in earlier tests was satisfactory cooling oil for most of the experiments. It was added only until conditions had become steady, after which the liquid level became self-sustained, and the composition remained constant.

In experiment 28 and part of experiment 29 a 250° to 350° C. cut of East White Lake crude oil was used to simulate proposed operation of the Bureau's Demonstration Plant. This oil reduced the activity of the catalyst. Presumably the sulfur content of this oil (0.06 percent) was sufficient to cause partial poisoning of the catalyst.

A low-boiling fraction (<250° C.) of Harnes oil was employed for the initial part of experiment 30, run in the barrel-per-day plant. In the subsequent test in this unit (experiment 31) neutralized reflux oil from the initial run served as coolant.

OPERATION AND DISCUSSION OF RESULTS

COMPARISON OF DATA FROM FIXED- AND EXPANDED-BED EXPERIMENTS

Data from selected periods of operation during both fixed- and expanded-bed tests are presented in table 18. For all the tests included, catalysts were first reduced with hydrogen, then inducted in the "stepwise" manner that was first used in experiment 12. By reference to this table, several important advantages will be shown to result from the expanded-bed method of operation (experiments 19, 22, and 26):

TABLE 18.—*Comparison of operation with oil-submerged, fixed and expanded beds*

[Average pressure, 300 p. s. i. g.]

Experiment No.	14-B	17-B	19-A, B, C	22-B	26-A
Mode of operation	Fixed		Expanded		
Catalyst:[1]					
Number	D-3006	D-3006	D-3006	D-3001	D-3001
Total age, hr.	2,300	2,360	2,670	2,356	1,604
Range of mesh sizes	4-6	4-6	6-16	6-20	6-20
Weight of iron, lb.	42.6	47.4	21.7	21.2	20.6
Volume (settled), cu. ft.	0.411	0.411	0.205	0.183	0.193
Height, ft.:					
Settled	8	8	4	4	4
Expanded	------	------	5.2	5.2	5.2
Oil, fresh makeup:					
Boiling range at 1 atm., °C.	250-350	------	------	------	------
Lb. per day	9.7	0.0	0.0	0.0	0.0
Synthesis gas:					
Ratio in fresh gas, H_2:CO	1.0	1.3	1.3	1.0	0.7
S. V. H.:					
Settled bed	292	302	601	602	602
Expanded bed	------	------	462	463	463
Flow, cu. ft. per hr. (S. T. P.)	121.7	124.0	123.2	110.2	110.2
Space-weight velocity of H_2+CO cu. ft. (S. T. P.) per hr. per lb. Fe	2.80	2.67	4.97	5.20	5.35
Conversion, vol.-percent:					
CO	72.7	78.6	79.8	70.5	66.0
H_2	67.3	64.2	63.0	65.9	69.5
H_2+CO	69.9	70.6	70.3	68.4	67.5
Space-weight conversion cu. ft. (H_2+CO) per hr. per lb. Fe	1.96	1.84	3.40	3.53	3.57
Usage ratio, H_2:CO	0.95	1.08	1.04	0.91	0.73
Gas-recycle ratio	2	1	1	1	1.4
Pressure: Differential, p.s.i.:					
Start of experiment	4	4	5	5	5
End of experiment	49	15	5	5	5
Temperature, °C.:					
Maximum	254-259	262-265	244-249	244	251
Differential	15	15	6	5	5
Yields, specific, gm. per m.³					
CH_4	17.6	18.3	14.7	19.0	14.3
C_2H_6	12.1	12.6	10.8	11.0	8.9
C_2H_4	2.4	3.8	5.7	4.6	6.3
C_3H_8	7.4	6.7	5.3	7.4	5.7
C_3H_6	14.6	17.4	18.5	8.5	11.7
C_4H_{10}	6.8	5.0	4.8	3.9	4.1
C_4H_8	11.9	12.1	13.2	14.1	11.6
C_5H_{12}	1.9	2.4	2.8	4.9	0.6
C_5H_{10}	6.5	6.8	8.4	11.5	11.3
C_6H_{14}	------	0.7	0.8	------	0.4
C_6H_{12}	------	1.3	2.4	8.3	0.5

See footnotes at end of table.

TABLE 18.—*Comparison of operation with oil-submerged, fixed and expanded beds*—Continued

[Average pressure, 300 p.s.i.g.]

Experiment No.	14-B	17-B	19-A, B, C	22-B	26-A
Mode of operation	←Fixed	→	←	Expanded	→
Yields, specific, gm. per m.³—Continued					
C_1+	-----	3.4	5.1	6.4	-----
C_1+, actual [3]	151.3	153.9	166.7	145.5	157.4
Space-time of C_3+, kg. per m.³ settled cat. vol. per day:					
Actual	740	783	1,685	1,456	1,518
Calculated	855	881	1,706	1,700	1,725
Products:					
Recovery, lb. per day:					
Heavy oil	7.32	6.87	7.90	5.41	7.92
Light oil	14.68	6.07	4.86	1.67	5.81
Reflux oil	-----	1.18	1.22	2.29	1.64
Charcoal spirits and gas	-----	[4] 0.45	[4] 0.67	[4] 0.72	-----
Aqueous layer	12.53	15.09	15.18	10.35	5.92
Distribution of C_3+, lb. per day: [5]					
Gasoline (C_3+)	11.54	[6] 13.10	13.55	9.40	9.24
Diesel oil	3.18	2.42	2.49	2.18	2.15
Heavy distillate	1.57	2.80	2.92	2.54	3.70
Wax	2.40	1.83	2.77	1.87	2.32
Distribution of C_3+, wt.-percent: [7]					
Gasoline (C_3+)	61.8	[6] 63.2	62.4	58.8	52.9
Diesel oil	17.0	12.6	11.5	13.6	12.3
Heavy distillate	8.4	14.6	13.4	15.9	21.5
Wax	12.8	9.6	12.7	11.7	13.3
Material balance, recovery percent	93.5	95.4	98.5	97.9	98.0

[1] Reduced with hydrogen and inducted stepwise.
[2] Recycled gas free of carbon dioxide.
[3] Does not include oxygenates in the aqueous layer; otherwise based on actual recoveries.
[4] C_3-C_4 material only. C_1-C_2 included in specific yields given.
[5] Net distribution after deducting feed oil; values include oil-soluble oxygenates.
[6] Corrected for theoretical removal of oxygenates.
[7] Not corrected for oxygenates.

1. Operating temperature was 10° to 15° C. lower, which should contribute appreciably to the life of the catalyst. The lower temperature of operation probably was made possible by the use of smaller catalyst particles that provided greater geometric surface area to the reacting gases.

2. Cementation was apparently completely avoided, as evidenced by the uniformly small pressure drop maintained up to more than 2,000 hours of operation. This result is made more striking by the fact that the catalyst, as charged, consisted of particles roughly one-eighth as large as were employed in fixed-bed experiments, a condition that unquestionably would have led to early shutdown if the bed had not been agitated. It should be emphasized that experiments 19, 22, and 26 were terminated voluntarily, whereas experiment 14 suffered forced shutdown because of excessive pressure drop, and experiment 17 was on the way to forced termination after 2,260 hours on stream.

3. Greatly increased throughputs and yields were realized as calculated on the basis of settled catalyst volume or weight of catalyst charged. For example, in experiment 19 the measured space-time yield was 1,685 kg. C_3+ per day per m.³ of catalyst, or more than twice the production realized in experiment 17. Feed-gas composition and total gas throughput were essentially identical in these two runs, but the space velocity attained in experiment 19 (based on settled catalyst volume) was twice as great as was maintained in experiment 17. From these results expanded-bed operation shows a 50-percent saving in catalyst cost.

Even though lower temperatures were used in the expanded-bed experiments, the relative amounts of gaseous and liquid hydrocarbons (gasoline, diesel oil, heavy distillate, and wax) were virtually the same as those observed in fixed-bed synthesis. The specific yield and product-distribution columns of table 18 illustrate this point. Normally, the production of gasoline and C_1 plus C_2 hydrocarbons decreases and the production of wax increases as the temperature is lowered.

Table 18 also includes data for a typical period of operation with $0.7H_2+1CO$ (experiment 26). Throughout this experiment, carbon dioxide was removed from the recycle gas, a procedure that usually has been found to allow a reduction in the reaction temperature of 5° to 10° C. However, no such improvement was obtained in this instance, as shown by the fact that the operating temperature required was as high as that maintained in experiments 19 and 22, in which carbon dioxide was not scrubbed out. Experiment 26 did show a slight decrease (2 to 5 gm. per m.³) in specific yield of C_1 plus C_2 hydrocarbons and a slight increase in heavier products; both effects were tentatively attributed to increasing the proportion of carbon monoxide in the feed gas.

In all experiments olefins predominated in the C_3 to C_6 range; conversely, the yield of ethylene was lower than that of ethane. As might be expected, the oils produced from

$0.7H_2+1CO$ were more unsaturated than those from either $1H_2+1CO$ or $1.3H_2+1CO$.

SIMULATED SECOND STAGE

The 70-percent conversion of synthesis gas in the experiments recorded in table 18 is not the maximum obtainable in single-stage converter operation. On the assumption, however, that it might never be found feasible to obtain substantially more than 70-percent conversion in a single stage, tests were conducted to simulate passing the tail gases from experiment 19–C through a second stage. The aim was to secure 90-percent over-all conversion by converting 70 percent of the hydrogen and carbon monoxide in this gas in the second stage.

For this series of tests the feed gas to the simulated second stage was a blended mixture based on the composition of the tail gas from experiment 19–C. As shown in table 18, the H_2:CO ratio in the feed gas throughout experiment 19–C was 1.3. The average usage ratio was 1.04, so that the H_2:CO ratio in the tail gas was approximately 2. Carbon dioxide content was roughly 25 percent, and nitrogen plus C_1 and C_2 hydrocarbons about 6 percent. In making up the synthetic mixtures the inerts and low-molecular-weight hydrocarbons were omitted, as it is reasonable to assume that they have no influence on the synthesis except as diluents, with little effect at such low concentrations. Carbon dioxide is not inert in the synthesis, so tests were conducted both in its complete absence and with its addition in the amount present in experiment 19–C. Feed-gas mixtures for the tests contained hydrogen and carbon monoxide in the 2:1 ratio present in experiment 19–C exit gases.

Data from these tests and also from experiment 19–C for comparison are presented in table 19. Significant results may be summarized as follows:

1. Unequal conversion of hydrogen and carbon monoxide in the first stage seems conducive to greater deviation of conversions in the second stage when carbon dioxide is absent from the second-stage feed gas, a condition representing operation with scrubbing between stages. When carbon dioxide is present in the second-stage feed gas, the utilization of the gas is similar in both stages.

2. Because conversion of carbon monoxide was relatively high and consequently the partial pressure of hydrogen was also relatively high in both experiments simulating second-stage operation, the production of C_1 plus C_2 hydrocarbons increased significantly. To avoid this, the composition of the first-stage feed gas must conform to the usage ratio. The data of table 18 will show that feed gas having a composition corresponding to $1H_2+1CO$ or perhaps slightly richer in carbon monoxide will make a close approach to meeting this requirement.

3. In high concentrations such as prevailed in experiment 19–D, part 2, carbon dioxide acts detrimentally and quickly reduces the activity of the catalyst to a level requiring reactivation. This experiment had to be terminated after 7 days' operation because of catalyst failure. Interstage removal of carbon dioxide thus seems essential to multistage operation.

TABLE 19.—*Comparison of first-stage with simulated second-stage operation*

Stage	First	Simulated second	Simulated second
Experiment No.	19 A, B, C	19-D (pt. 1)	19-D (pt. 2)
Synthesis gas:			
Ratio in fresh gas, H_2:CO	1.3	2.0	2.0
S. V. H. (settled bed)	601	601	[1] 625
Flow ft.³ per hr. (S.T.P.)	123.2	122.0	129.0
CO_2 added ... do.	0	0	41.0
CO_2 added, vol.-percent	(2)	(2)	25.0
Conversion, vol.-percent:			
CO	78.5	87.9	77.8
H_2	64.0	62.7	67.4
H_2+CO	70.3	70.8	70.4
Usage ratio, H_2:CO	1.14	1.46	1.36
Gas-recycle ratio	1	1	1
Pressure, average p. s. i. g.	300	300	300
Temperature, maximum °C.	246	251	274
Yields, specific gm. C_1+C_2 per m.³ [1]	31.2	40.0	40.3

[1] Based on H_2+CO only.

[2] Carbon dioxide content of synthesis gas, 0.1 volume percent.

HIGH SPACE VELOCITY

Synthesis at increased throughputs (hourly space velocities up to 1,000) was studied in experiments 21–A and 22–B. Experiment 21–A consisted of several comparatively short tests conducted to determine whether detrimental effects that could be detected rapidly might accompany high conversions at high throughputs. Results were encouraging, as shown in table 20. Suitably high overall conversion (up to 70 percent) was readily attained at reasonable (although higher) temperatures. There seemed to be some increase in C_1 and C_2 hydrocarbons in the product, but the magnitude of this effect was not great. Product-distribution analyses (table 21) showed a significant increase in gasoline that could probably be attributed to the increased temperature rather than to increased throughput; at the same time there was a decrease in heavy distillate.

A more extended study at high throughput was made in experiment 22–B, but at a converter pressure of 400 rather than 300 p. s. i. g. In the early part of this test, production and general performance were similar to experiment 21; that is, about 70-percent conversion was obtained at somewhat higher but still reasonably low temperatures (table 22). Despite the substantial increase in temperature that was necessary to maintain a 70-percent conversion in going from an hourly space velocity of 600 to 1,000 in experiment 22 B, gasoline production increased only slightly, and yields of C_1 plus C_2 hydrocarbons remained about the same. Catalyst activity decreased so rapidly over a 12-day period at the high gas throughput that the experiment was terminated.

TABLE 20.—*Effect of space velocity on synthesis with reduced fused iron in experiment 21-A*

Test No.[1]	1	2	3	4	5
Duration, hr.	148	5	38	4	48
Synthesis:					
Ratio in fresh gas, H_2:CO	1.3	1.3	1.3	1.3	1.3
S. V. H. (settled bed)	600	800	800	1,000	1,000
Flow, ft.³ per hr. (S.T.P.)	123.4	164.9	163.9	205.0	207.5
Conversion, vol.-percent H_2+CO	70.8	66.3	64.3	57.8	60.3
Usage ratio, H_2:CO	1.13	1.28	1.19	1.16	1.05
Gas-recycle ratio		1	1	1	1
Pressure:					
Maximum, p. s. i. g.	307	300	300	311	311
Differential, p. s. i.	3	5	3	4	8
Temperature, °C.:					
Average	234	231	239	250	248
Differential	6	8	9	9	11
Yields, specific, C_1+C_2 gm. per m.³	27.4	22.2	28.8	32.3	33.0

[1] Without removal of carbon dioxide.

TABLE 21.—*Distribution of C_5+products at high hourly space velocities with $1.3H_2$+1CO and reduced fused iron in experiment 21-A*

Test No.	(1)		(5)	
	Lb. per day[1]	Wt.-percent	Lb. per day[1]	Wt.-percent
Gasoline (C_5—)	[2] 13.20	58.9	[3] 22.15	66.8
Diesel oil	2.68	12.0	3.94	11.9
Heavy distillate	3.80	17.0	3.51	10.6
Wax	2.72	12.1	3.55	10.7
Total C_5+ products	22.40	100.0	33.15	100.0

[1] Includes oil-soluble oxygenates.
[2] Actual charcoal recovery included.
[3] Calculated charcoal recovery included.

TABLE 22.—*Data for synthesis at high hourly space velocities in experiment 22-B*

Duration of test, days	3	12
Bauxite[1] reactor temperature, °C.	370	[2] 370
Synthesis gas:		
Ratio in fresh gas, H_2:CO	1.0	1.0
S. V. H. (settled bed)	600	1,000
Flow, cu. ft. per hr. (S. T. P.)	110.4	182.6
Conversion, vol.-percent H_2+CO	66.1	67.2
Usage ratio, H_2:CO	1.06	0.99
Gas-recycle ratio[3]	1	1
Pressure, average, p. s. i. g.	400	400
Temperature, °C.:		
Maximum	236	254-263
Differential	6	7
Yields, specific, C_1+C_2, gm. per m.³	32.6	27.4
Products, distribution of C_5+, wt. percent:[4]		
Gasoline (C_5+)	57.5	59.7
Diesel oil	12.2	13.1
Heavy distillate	14.5	12.9
Wax	15.8	14.3

[1] Alumina "F-1" catalyst, supplied by Aluminum Co. of America.
[2] Reactor in intermittent service.
[3] Tests without removal of carbon dioxide.
[4] Oil-soluble oxygenates are included.

HIGH CONVERSION, WITHOUT REMOVAL OF CARBON DIOXIDE

In the preceding experiments 70-percent conversion of gas was maintained, a value that appeared to be acceptable performance for the first stage of a 2-stage process in which 91 percent over-all conversion would be attained. To determine whether as much as 90-percent conversion could be achieved in a single-stage operation, experiment 23-B was conducted; the temperature was increased and the effect on conversion observed. To establish a baseline of performance at "standard" operating conditions the first period of operation in this experiment was conducted at 70-percent conversion of $1H_2$+1CO at an hourly space velocity of 600, a pressure of 300 p. s. i. g., and a gas-recycle ratio of 1, without removal of carbon dioxide; a temperature of 243° C. was required. A 20° C. increase in temperature resulted in 85-percent conversion, but further increases to 295° C. did not increase the conversion beyond 85 percent (table 23 and fig. 14). A slight improvement in usage ratio resulted when the recycle ratio was increased from 1 to 2, but no gain in conversion was noted. Therefore, 85-percent conversion appears to have lowered the H_2+CO content of the gas so much that their partial pressures were too low for further reaction in single-stage operation. Another possibility is that the desorption of carbon dioxide, the concentration of which rose to about 45 to 50 percent, was quite slow and therefore a rate-determining factor.

Apparently the high temperatures that are necessary to secure high conversion quickly lowered the activity of the catalyst. After approximately 250 and 300 hours under these extreme conditions, increases of 25° and 34° C., respectively, were required for 70-percent conversion. Throughout the tests the specific yields of gaseous hydrocarbons increased with temperature, rising to over 50 gm. per m.³

HIGH CONVERSION, WITH REMOVAL OF CARBON DIOXIDE

Experiment 23-B indicated that the minimum overall synthesis-gas conversion of 90 percent, which must be achieved in an acceptable process, is not likely to be realized only by increasing the operating temperature. It is certain that the substantial concentrations of carbon dioxide produced by the synthesis have a diluent effect and probably also, by partial oxidation of the catalyst, interfere with the reaction. Acting upon these premises, experiments were conducted in which the carbon dioxide content of the converter system was substantially reduced by a continuous scrubbing operation applied to the gas-recycle stream. Initially, 3 half-hour tests (hourly space velocity of 600, $1H_2$+1CO, 1:1 recycle ratio, 247° C., 300 p. s. i. g.) were made (experiment 22-C) in which carbon dioxide was removed by water scrubbing (see fig. 12, p. 34). The concentration of carbon dioxide was reduced from approximately 15 percent to 6. Twenty-five to thirty

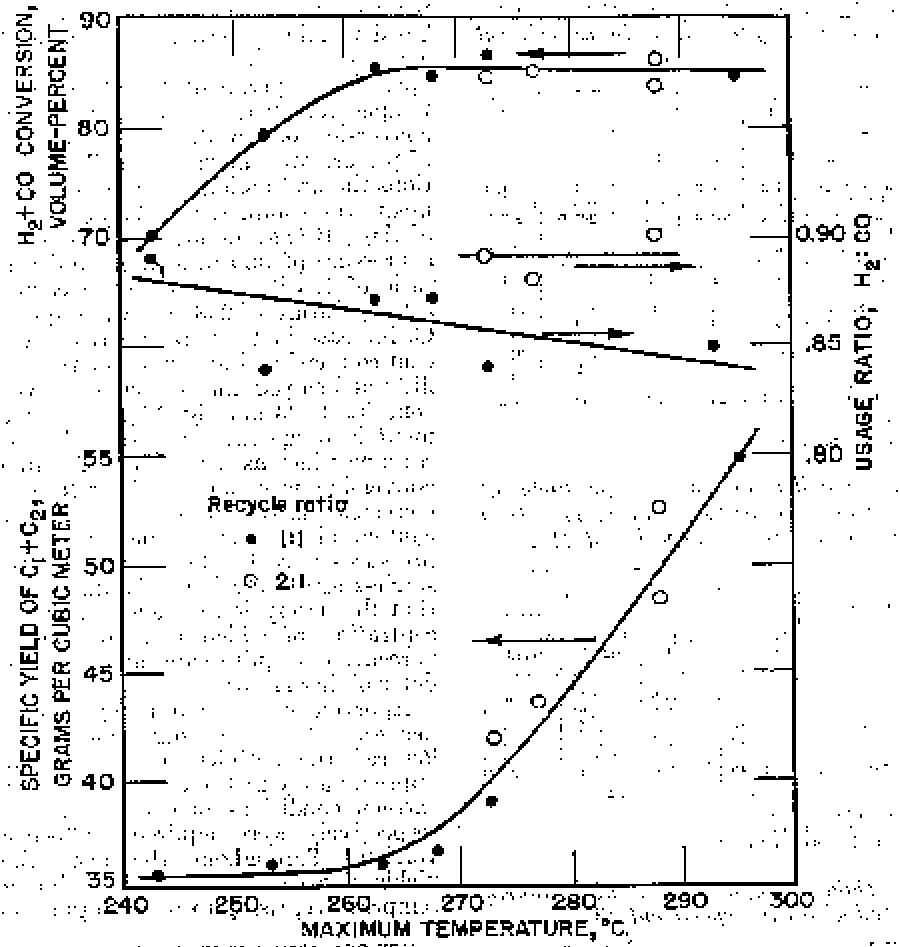

FIGURE 14.—Effect of Temperature on Synthesis Without Removal of Carbon Dioxide (Hourly Space Velocity, 600).

TABLE 23.—*Effect of temperature on conversion (without removal of carbon dioxide) in experiment 23–B*

[Synthesis gas ratio in fresh gas, H_2:CO, 1.0; S. V. H. (settled bed), 600; pressure, average—300 p. s. i. g.]

Test No.	1	2	3	4	5	6	7	8	9	10	11	12
Catalyst age for period hr.	1,086–1,133	1,136–1,157	1,160–1,185	1,188–1,234	1,241–1,277	1,285–1,301	1,304–1,316	1,338–1,360	1,366–1,386	1,405–1,420	1,425–1,444	1,455–1,470
Synthesis gas:												
Conversion vol.-percent H_2+CO	71.0	79.4	85.2	84.1	86.3	84.2	85.4	86.0	71.3	83.7	84.4	71.8
Usage ratio, H_2:CO	0.89	0.84	0.87	0.87	0.84	0.89	0.88	0.90	0.80	0.90	0.85	0.88
Gas recycle ratio	1	1	1	1	1	2	2	2	1	2	1	1
Temperature, maximum °C.	242	253	263	268	273	273	277	288	[2] 248	288	295	[3] 247
Yields, specific C_1+C_{21} gm. per m.³	35.5	35.9	36.0	36.0	39.3	41.9	43.6	48.4	43.3	52.7	54.8	47.9

[1] Normal operation.
[2] Temperature decreased to check activity after 250 hours.
[3] Temperature decreased to check activity after 300 hours.

percent of carbon dioxide is normally present in the recycle gas during operation at 70-percent conversion without scrubbing. Scrubbing of gas increased the conversion from 70.8 percent to 79 under otherwise similar conditions of synthesis. A calculated concentration of 40 to 42 percent would have prevailed at 79-percent conversion without scrubbing.

However, about 10 percent of the synthesis gas was lost by solution in the water that was circulated at a rate of 280 to 300 gallons per hour (about 2 gal. per ft.^{3} of gas feed). Since this loss was prohibitive, the system was revised during experiment 22-C (see fig. 13, p. 35) so that 15-percent aqueous potassium carbonate solution could be used instead of water. The rate of pumping was thereby lowered to about one-tenth that needed for water. Consequently, the loss of synthesis gas amounted to to less than 0.5 percent of the fresh gas.

The experiments in which potassium carbonate was used are summarized in table 24. Data have been grouped in the following order:

1. Effect of removal of carbon dioxide from recycle gas at constant temperature and space velocity.
2. Effect of removal of carbon dioxide at constant conversion and space velocity.
3. Effect of temperature and removal of carbon dioxide on conversion at constant space velocity.
4. Effect of removal of carbon dioxide at space velocities of 600 to 900.
5. Effect of temperature and removal of carbon dioxide on conversion at space velocity higher than in (3).

Except for experiment 26, in which carbon dioxide was scrubbed throughout the entire run (1,504 hours), carbon dioxide was removed only for short periods. Therefore, complete product distributions were usually not obtained. However, the specific yields of C_1 plus C_2 hydrocarbons are always given.

Group (1) of table 24 shows that an increase of about 10 percent in conversion is gained by removal of carbon dioxide when the H_2:CO ratio in the fresh gas lies between 0.7 and 1. A 75-percent conversion at a space velocity of 600 with $1H_2+1CO$ could probably be attained without scrubbing. However, synthesis probably could not be sustained at this level without scrubbing if $0.7H_2+1CO$ were used at the same space velocity because the concentration of carbon dioxide would be 47 volume-percent or higher.

A further advantage of removing carbon dioxide shown in group (1) tests was the lower yield of C_1 plus C_2 hydrocarbons, except in tests 1 and 2 of experiment 24 A, in which sulfur contamination was suspected. Reductions in the specific yield of these gases by 8 to 10 and 3 to 4 gm. per m.^{3} were obtained with $1H_2+1CO$ and $0.7H_2+1CO$, respectively. This decrease reflects a gain in C_3+ production at a given temperature.

Group (2), table 24, shows that the temperature needed for a given conversion is lower when carbon dioxide is removed. An 8° C. drop was attained in this case, equivalent to a possible gain of 6 to 8 weeks of synthesis.

Scrubbing was employed in all group (3) tests. Temperature increases of 12° to 17° C. resulted in increasing the conversion from about 70 to 90 percent in every case. Figure 15 shows that the rise in conversion with increasing temperature was linear and that the slopes of the lines for the several experiments were similar. As expected, the usage ratios declined with rising temperatures. These tests were long enough to indicate that high conversion in a single stage is feasible for long periods if carbon dioxide concentration is maintained at a low level.

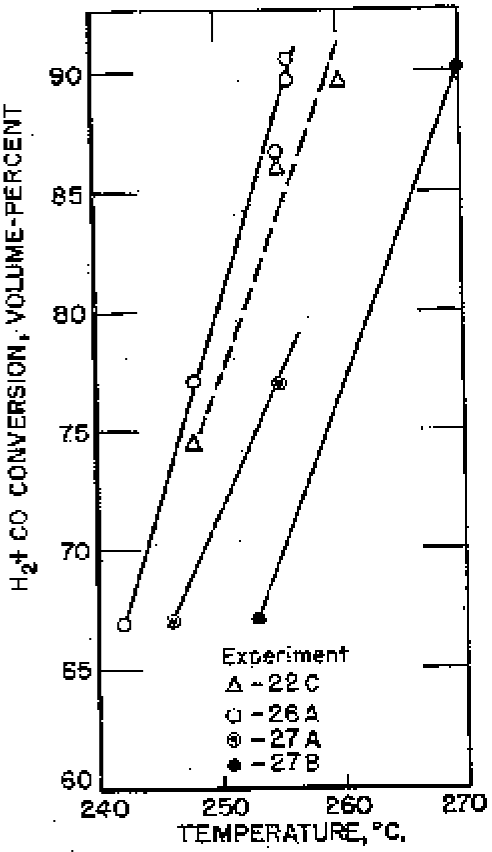

FIGURE 15.—Effect of Temperature on Conversion With Removal of Carbon Dioxide (Hourly Space Velocity, 600).

Examination of groups (4) and (5) shows that an increase in the space velocity from 600

TABLE 24. *Summary of tests on removal of carbon dioxide from recycle gas*

	(1) Effect of removal of carbon dioxide at constant temperature at 600 S. V. H.										(2) Constant conversion		(3) Effect of temperature and removal of carbon dioxide at 600 S. V. H.		
Experiment No.	23-C¹					24-A			27-A		27-A		33-C¹		
	Operation without scrubber	Test 1	Test 3	Operation without scrubber	Test 4	Operation without scrubber	Test 1	Test 9	Operation without scrubber	Test 5	Operation without scrubber	Test 4	Test 2	Test 3	Test 4
Duration of test...hr..	34	2	2	4	4	24	3	6	22	13	22	88	2	2	2
Catalyst age, start of test...do...	2,024	2,053	2,065	2,144	2,148	434	513	518	157	266	185	317	2,056	2,060	2,086
Bauxite-reactor temperature...° C..	325	325	326	325	320	(2)	(2)	(2)	(2)	(2)	(2)	(2)	325	325	320
Synthesis gas:															
Ratio in fresh gas, H_2:CO...	1.0	1.0	1.0	1.0	1.0	0.7	0.7	0.7	0.7	0.7	0.7	0.7	1.0	1.0	1.0
S. V. H. (settled bed)...	600	600	600	600	600	600	600	660	603	632	602	662	800	400	600
Conversion...vol.-percent H_2+CO...	68.2	73.7	74.8	73.0	68.1	67.0	75.4	75.9	67.2	77.1	[illegible]	87.0	71.6	86.0	84.6
Convertibility (S. V. H.×conversion fraction)...	409	442	448	438	409	402	452	482	404	488	475	540	555	616	538
Usage ratio, H_2:CO...	1.02	0.98	1.00	0.98	0.94	0.89	0.63	0.72	0.78	0.78	0.78	0.80	1.00	0.96	1.04
Gas-recycle ratio...	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Pressure, average...p. s. i. g...	400	400	400	400	400	300	500	300	400	400	400	400	400	400	400
Temperature, ° C.:															
Maximum...	248	246	245	255	250	250	278	288	254	256	254	248	248	265	260
Differential...	8	5	9	7	7	8	8	8	2	3	3	2	8	10	0
Yields, specific...gm. C_3+C₂ per m.³...	37.7	25.7	30.1	47.3	40.0	31.8	³27.5	³30.9	23.7	16.0	21.7	15.0	30.3	32.2	10.6
CO_2 content of gases, vol.-percent:															
Tail gas without scrubbing:															
Measured...	24.9	-------		26.8	-------	32.6	-------	-------	30.6	-------	30.6	-------	-------	-------	-------
Calculated...	-------	33.6	33.0	-------	15.0	-------	46.5	47.0	-------	46.0	-------	21.5	33.0	52.0	61.0
Recycle gas into scrubber...	-------	13.0	13.0	-------	14.1	-------	18.5	14.8	-------	14.6	-------	14.6	13.6	16.0	16.8
Scrubbed gas...	-------	1.0	1.3	-------	5.6	-------	5.7	4.2	-------	4.2	-------	1.2	1.3	8.0	3.4

[1] Activated alumina "F-1", supplied by Aluminum Co. of America, 4 to 8-mesh, used in bauxite reactor.

[2] Reactor out of service.

[3] Suspected sulfur contamination.

TABLE 24.—*Summary of tests on removal of carbon dioxide from recycle gas*—Continued

	(3) Effect of temperature and removal of carbon dioxide at 600 S. V. H.—Continued									(4) Convertibility						(5) Effect of temperature and removal of carbon dioxide at 900 S. V. H.					
Experiment No.	26-A [1]					27-A		27-B		26-A [1]		27-A		27-B		28-A [1]		28-B [4]			
	Test 2	Test 3	Test 4	Test 5 [2]	Test 7	Test 4	Test 5	Test 9	Test 10	Test 7	Test 8	Test 5	Test 6	Test 10	Test 11	Test 8	Test 9 [5]	Test 11	Test 12	Test 14	Test 14
Duration of test ... hr.	41	46	96	68	304	88	18	9	128	210	48	15	46	123	40	46	44	10	23	58	6
Catalyst age, start of test ... hr.	268	303	364	456	595	317	345	635	680	890	920	506	328	689	812	930	971	1,245	1,351	1,378	1,462
Bauxite-reactor temperature ... °C.	325	326	325	335	[3] 332	(5)	(4)	(3)	(7)	[3] 330	(2)	(2)	(2)	(1)	(2)	(4)	(4)	300	200	300	300
Synthesis gas:																					
Ratio in fresh gas, H_2:CO	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
S. V. H. (settled bed)	598	589	593	599	600	603	582	601	608	600	603	592	748	803	900	898	885	909	937	894	897
Conversion, vol.-percent H_2+CO	34.9	77.2	80.7	50.6	88.7	87.0	77.1	88.9	90.2	80.7	65.0	77.1	48.1	90.2	44.1-56.4	85.0	83.7	69.8	86.5	87.7	89.2
Convertibility (S. V. H. × conversion fraction)	404	468	617	649	533	403	456	403	611	538	580	456	508	544	477-508	680	740	626	773	784	701
Usage ratio, H_2:CO	0.74	0.72	0.69	0.68	0.65	0.80	0.72	0.81	0.71	0.58	0.73	0.78	0.77	0.70	0.89	0.74	0.80	0.78	0.88	0.79	0.89
Gas-recycle ratio	3	1	1	1	1-1.5	1	1	1	1	1-1.5	1	1	1	1	1	1	1	1	1	1.5	1.6
Pressure, average ... p. s. i. g.	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400	400
Temperature, °C.:																					
Maximum	252	248	265	268	258	246	266	253	273-280	266	262	265	256	273-283	269	263	276	265	266	271	281
Differential	5	5	5	6	6	2	3	8	4	8	5	3	2	4	8	6	6	5	8	7	7
Yields, specific gm. C_3+C_4 per m.^{3}	24.8	28.1	30.6	26.4	21.6	18.9	19.0	19.0	25.3	25.4	23.2	10.0	21.3	23.7	19.2	23.3	35.2	30.1	37.2	30.5	34.2
CO_2 content of gases, vol.-percent:																					
Tail gas without scrubbing:																					
Measured																					
Calculated	32.6	44.0	63.6	71.0	70.6	31.0	45.0	31.0	70.0	70.0	61.0	45.0	33.0	75.0	37.0-21.0	31.0	57.0	35.6	62.6	66.0	66.0
Recycle gas into scrubber	11.9	15.0	13.9	20.0	18.1	11.5	14.4	11.2	19.9	18.1	17.8	14.6	12.3	19.6	10.7-7.9	12.6	18.7-14.0	14.7	20.6	18.7	17.6
Scrubbed gas	7.0	6.0	4.6	3.1	3.4	1.2	11.2	1.6	2.8	3.4	4.3	0.2	7.7	2.6	1.6	4.6	[5] 11.2-8.1	1.6	3.4	8.8	2.6

[1] Phillips Cycloceel bauxite, 4- to 12-mesh, used in bauxite reactor.

[2] Activity check at 600 S. V. H. and 70-percent conversion in test 6 showed activity unimpaired by operation at high conversion.

[4] Activity check at 600 S. V. H. and 70-percent conversion in test 10 showed that a 5° C. increase was required.

[3] Reactor in intermittent service.

[5] Potassium carbonate flow increased from 40 to 60 gal. per hr.

to 900 at constant temperature resulted in lowering the conversion from 90 percent to about 65. On a convertibility basis (product of hourly space velocity and fraction converted), a small gain of about 8 percent was attained at the faster flow. The usage ratio increased at these higher flow rates, probably because of the smaller conversion per pass. Yields of C_1 plus C_2 hydrocarbons declined. The activity decreased rapidly at 900 space velocity in test 11. A simultaneous sharp increase of the iron content in the recycle oil (from 0.05 percent to 1.39) indicated that some of the active material had been removed from the catalyst either by mechanical or chemical action or by both.

Experiment 37–A (group 4) demonstrated that, in addition to a 10-percent gain in convertibility due to scrubbing of carbon dioxide, a further gain of about 15 percent resulted at the same temperature from increasing the space velocity so that only 70-percent conversion was attained. The hourly space velocity of fresh feed could be boosted from 600 (without scrubbing) to 750 (with scrubbing) while 70-percent conversion was maintained (test 6). Although operation at the higher gas rate and 70-percent conversion appears more desirable because of the resultant greater space-time yields, a longer test would be required to study the effect of such operation on catalyst life.

Tests 9, 12, 13, and 14 in group (5) were relatively brief but showed rather conclusively that 90-percent conversion at a space velocity of 900 with $0.7H_2+1CO$ is not to be expected with the fused iron (D–3001) employed, even though carbon dioxide is maintained at a low level. After operation at 275° C. for about 2 days (test 13), the activity declined so rapidly that increases of 8° to 10° C. per day were required to maintain 90-percent conversion; after 3 more days the temperature had to be raised to 293° C. By that time loss of catalytic activity was so great that the experiment had to be terminated.

PRESSURE EFFECT

To determine whether higher pressures are advantageous, synthesis was conducted at 400 p. s. i. g. Comparative data for operation at 300 and 400 p. s. i. g. are given in table 25 for $1H_2+1CO$ and $0.7H_2+1CO$. At the higher pressure, the temperature could be reduced by 3° to 8° C., from which it may be deduced that the synthesis shows a positive pressure coefficient in this range as well as at lower pressures. The specific yield of C_1 plus C_2 hydrocarbons was lowered by 4 to 9 gm. per m^3. Although the usage ratio rose considerably (from about 0.93 to 1.05) with $1H_2+1CO$, it changed insignificantly (from 0.73 to 0.74) with $0.7H_2+1CO$ for the same pressure rise. This latter result is to be expected because the usage ratio slightly exceeded that of the feed gas even at the lower pressure.

An undesirable shift in product distribution toward heavier material was noted in all tests at higher pressures. This shift was more pronounced with $0.7H_2+1CO$ feed gas; the gasoline fraction was reduced substantially compared with the change observed with $1H_2+1CO$. Because the bauxite reactor was used in these

TABLE 25.—*Effect of pressure on operation and products from Fischer-Tropsch synthesis*

Experiment No.	22–B	22–B	22–C	22–C	26–A	26–A
Duration, hr.	72	48	24	48	168	48
Bauxite reactor temperature, °C.	[1] 370	[1] 370	[2] 325	[2] 325	[2] 325	[2] 325
Synthesis gas:						
Ratio in fresh gas, H_2:CO	1.0	1.0	1.0	1.0	0.7	0.7
S. V. H. (settled bed)	602	603	602	600	602	601
Flow, cu. ft. per hr. (S. T. P.)	110.2	110.4	110.3	109.8	110.2	110.1
Conversion, vol.-percent H_2+CO	67.3	66.1	66.4	68.0	67.5	66.9
Usage ratio, H_2:CO	0.92	1.03	0.94	1.08	0.73	0.74
Gas-recycle ratio	[3] 1	[3] 1	[4] 1	[4] 1	[4] 1	[4] 1
Pressure, average, p. s. i. g.	300	400	300	400	300	400
Temperature, ° C.:						
Maximum	244	236	244	241	251	242
Differential	5	6	7	5	5	5
Yields, specific C_1+C_2, gm. per m^3	38.1	32.4	42.4	33.1	29.6	24.8
Products, distribution of C_3+, wt.-percent:[5]						
Gasoline (C_4+)	58.6	57.5	66.1	61.4	52.9	43.2
Diesel oil	12.5	13.2	13.7	13.7	12.3	15.6
Heavy distillate	19.3	15.5	11.6	16.0	21.5	19.9
Wax	9.6	13.8	8.6	8.9	13.3	21.3

[1] 4- to 8-mesh activated alumina "F-1", supplied by Aluminum Co. of America.
[2] 4- to 12-mesh Phillips Cyclocel.
[3] Without removal of carbon dioxide.
[4] With removal of carbon dioxide.
[5] Includes oil-soluble oxygenates.

tests, no change was noted in the amounts of oxygenated compounds. However, at the higher pressure slightly more oxygenated material may have been synthesized.

CATALYSTS FROM FEDERAL BUREAU OF MINES DEMONSTRATION PLANT

Experiments 28 and 29 were made to evaluate catalysts prepared at the Bureau's demonstration plant at Louisiana, Mo. These catalysts are analyzed in table 26, along with the composition of catalyst D–3001 used almost exclusively in the Bruceton pilot-plant studies. The Louisiana catalysts were similar to catalyst D–3001, except that they contained more ferrous iron; also, Louisiana 8 contained no chromic oxide.

Because the East White Lake crude oil used as coolant in experiment 28 was suspected of causing sulfur poisoning, no direct comparison can be made between the activity of catalyst 8 from Louisiana and that of catalyst D–3001; dry-bed tests indicated that the activities were about the same.

Experiment 29 showed that the activity of Louisiana catalyst 9 was slightly inferior to that of catalyst D–3001 under comparable conditions. Initially, 56-percent carbon dioxide-free contraction was observed at 260° C. (gas composition $0.7H_2+1CO$, hourly space velocity 600, pressure 300 p.s.i.g., gas-recycle ratio of 1 without removal of carbon dioxide), compared with 60- to 65-percent contraction observed in experiments 24, 25, and 27 under similar conditions with catalyst D–3001. However, catalyst 9 appeared to be more stable. No special pretreatment was given Louisiana catalyst 9, whereas catalyst D–3001 had been either precarbided (experiments 24 and 25) or pretreated with hydrogen-rich gas at low pressure (experiment 27).

TABLE 26.—*Chemical analyses of promoted, fused-iron oxides*

(Weight-percent)

	Catalyst D–3001	Louisiana, Mo.	
		Catalyst 8	Catalyst 9
FeO	27.36	50.84	59.97
Fe_2O_3	65.11	42.49	32.56
MgO	4.61	4.59	5.53
SiO_2	.71	.94	.56
K_2O	.67	.59	.33
Cr_2O_3	.65	----------	.70

The most noticeable difference between the catalysts was in the gas yields; specific yields of C_1 plus C_2 hydrocarbons averaged 40 to 45 grams for Louisiana catalyst 9 and 23 to 27 grams for catalyst D–3001. More gaseous hydrocarbons were obtained with Louisiana catalyst 9 in the dry-bed test also. Its lower alkali content may have caused the excessive gas yields. Owing to the brevity of the tests, no attempt was made to check the yields of liquid or compute product distributions; however, as might be expected from the high gas yields, the average molecular weight of the liquid products was lower than for those obtained with catalyst D–3001.

Both Louisiana catalysts became more highly carbided during synthesis than the commercial catalysts, and carbide was retained for a longer period. During experiment 29, 60 to 75 percent of the total iron in Louisiana catalyst 9 was present as Hägg iron carbide. After 470 hours of experiment 28, X-ray and magnetic analyses showed that Louisiana catalyst 8 consisted of 92 percent Hägg iron carbide, 8 percent metallic iron, and no magnetite. This was the largest amount of Hägg carbide found in a catalyst discharged from the oil-circulation units. The used commercial catalysts contained mostly magnetite, but also carbide and iron.

Louisiana catalyst 8 was extremely resistant to mechanical disintegration. During 470 hours of operation at 250° to 260° C. the circulating cooling oil remained light in color and contained only 0.007 to 0.035 percent iron. Virtually no fines were collected in the filter in the oil-circulating line, indicating that the particles were not being reduced in size. A sieve analysis of a representative sample of discharged catalyst also showed only a small amount of fines.

Virtually no spalling of catalyst was observed with Louisiana catalyst 9 during operation in the temperature range 262° to 267° C. However, after 5 days of synthesis at 275° C., 3 pounds of fines (about 11 percent of the original charge) was removed from the filter in the oil-circulating line. After 5 more days, the experiment had to be terminated because of excessive loss of activity; at that time 3 more pounds of fines was recovered in the filter. A sieve analysis of the used catalyst confirmed the fact that severe attrition had accompanied operation at 275° C. Thus, it appears that operation at temperatures above approximately 270° C. should be avoided for fused iron catalysts.

SPECIAL TESTS AND DISCUSSION OF RESULTS

USE OF STRIPPING COLUMN DURING SYNTHESIS

When $1.3H_2+1CO$ feed gas was employed with fused iron catalysts submerged in oil (experiments 17–A–B, 19–A–B–C–E–F–G, 20–A–B–C, 21–A) the usage ratio of hydrogen to carbon monoxide was less than the ratio in the feed. It has already been pointed out (see Simulated Second Stage, p. 38) that balanced usage is an especially important requirement in a multistage process to obtain high over-all gas conversion, to insure that product distribution does not vary from stage to stage, and especially to avoid excessive production of C_1 plus C_2 hydrocarbons after the first stage.

Excessive usage of carbon monoxide means in effect that the synthesis proceeds predominantly by the overall equation:

$$2\ n\text{-}CO + n\text{-}H_2 \rightarrow (CH_2)_n + n\text{-}CO_2,$$

so that carbon dioxide is the medium of oxygen elimination. There is evidence that this reaction takes place in two steps, according to the equations:

$$n\text{-}CO + 2\ n\text{-}H_2 \rightarrow (CH_2)_n + n\text{-}H_2O,$$
$$n\text{-}H_2O + n\text{-}CO \rightarrow n\text{-}CO_2 + n\text{-}H_2,$$

thus pointing to the occurrence of the water-gas shift as a secondary reaction and as the mechanism by which carbon dioxide is produced.

The most obvious means for preventing or minimizing the occurrence of the water-gas shift is reduction of the partial pressure of water vapor in the reactor. In experiments with $1H_2+1CO$ feed gas, satisfactory results were obtained by using a gas-recycle ratio between 1 and 3, and by cooling the recycle gas to a temperature (5° C.) where much of the water vapor was condensed and removed. On the other hand, in the experiments in which the composition of the feed gas corresponded to the ratio, $1.3H_2$:1CO, increasing the recycle ratio to as high as 6:1 did not correct the usage ratio sufficiently. (See Effect of Recycle Ratio on Yields of C_1 Plus C_2 Hydrocarbons and on Usage Ratio, p. 51.)

An apparent explanation for the low usage ratio was the fact that enough water dissolved in the circulating oil to produce the shift reaction. The presence of an appreciable amount of dissolved water was established during experiment 20-C with $1.3H_2+1CO$ feed gas, by reducing the pressure above a sample of the recycle oil from 300 to 0 p. s. i. g. and passing the released gases through a magnesium perchlorate drier.

As a possible method of further reducing the concentration of dissolved water during synthesis, the pilot plant was modified for experiment 23 to include a "stripping" column 6 inches in diameter packed with ½-inch ceramic Raschig rings to a height of 6 feet. The converter and stripping column were connected in parallel, as shown in figure 16. With this arrangement a mixture of dry fresh gas and recycle gas could be injected into the bottom of the converter while additional dry recycle gas could be simultaneously injected into the bottom of the stripping column and flow upward through a countercurrent stream of circulating oil to remove or "strip" dissolved water. Recycle gas not absorbed by the oil, stripped gas, and exit gas from the converter could then be passed from the top of the stripping column into a water-cooled condenser (operated at 40° to 45° C.) to remove most of the water. After

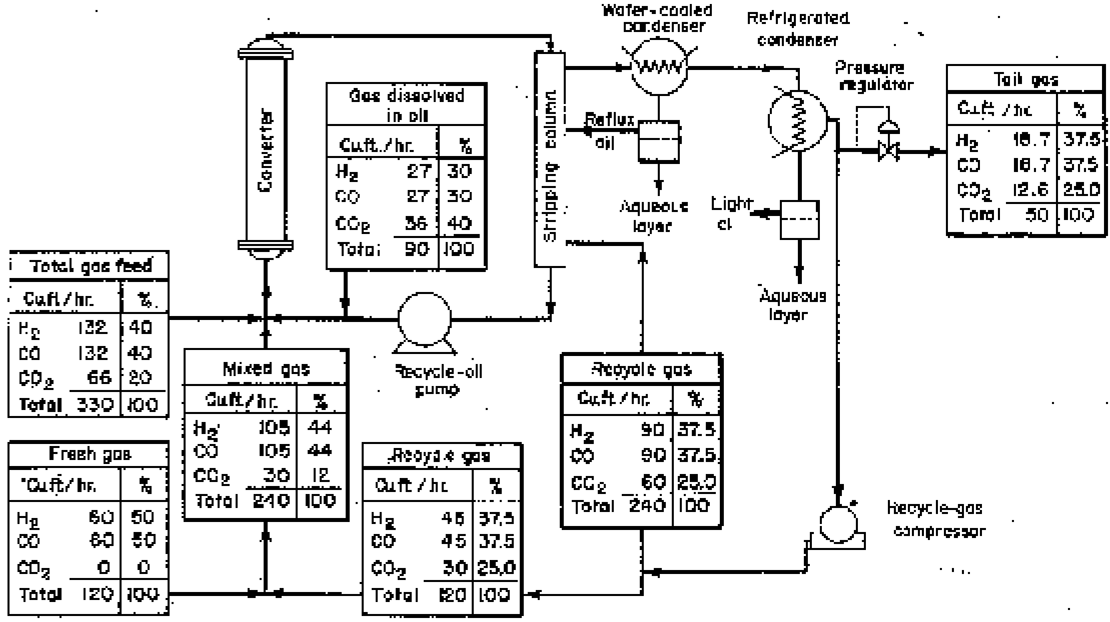

FIGURE 16.—Operation of Stripping Column in Parallel With Internally Cooled Converter Unit 1 During Experiment 23.

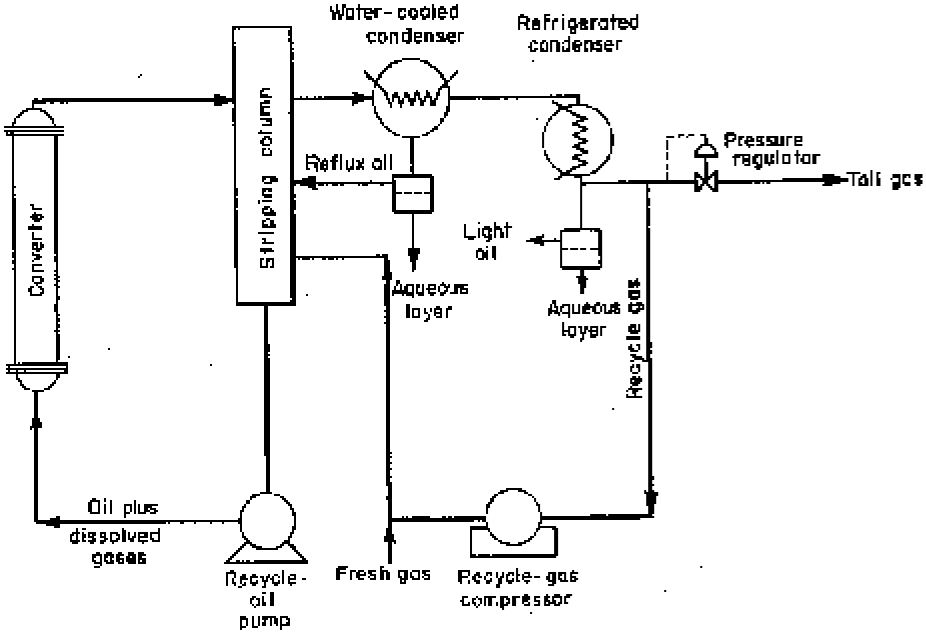

FIGURE 17.—Operation of Stripping Column With Internally Cooled Converter Unit 1, With All Gas Passing Through Column Only.

additional drying in a refrigerated condenser (operated at 5° C.) part of this gas could be recycled.

Before the plant was operated in the manner just described, a satisfactory catalyst activity was established at an hourly space velocity of 600 with $1H_2+1CO$, a gas recycle of 1, and a pressure of 300 p. s. i. g., and a special test was conducted with the stripping column. In this test all the gas (fresh plus recycle) was injected into the column (fig. 17). A maximum conversion of only 45 to 50 percent was obtained at 255° C., and the usage ratio was very low, for example, 0.75 at 32-percent conversion. By reducing the pressure above a sample of recycle oil and collecting the gas evolved, it was found that about 4 to 5 volumes of gas (S. T. P.), consisting essentially of 75 percent synthesis gas and 25 percent carbon dioxide (dry basis), was dissolved in each volume of oil. Carbon dioxide and water were much more soluble in the oil than was carbon monoxide; carbon monoxide was more soluble than hydrogen. This information agreed with data obtained in a similar manner during normal synthesis in experiments 17–A, 17–B, 19–G, and 20–C.

Calculations showed that, of 120 cubic feet of fresh synthesis gas injected hourly into the stripping column in this test, only about 75 to 80 cu. ft. per hr. dissolved in the oil circulating at a rate of 150 gal. per hr. and reached the converter. The rest of the gas passed overhead from the stripping column. Because of this limited solubility, over-all conversion of fresh gas was low (45 to 50 percent), even though approximately 80 percent of the gas entering the reactor was converted. Since conversion of the gas actually entering the converter was higher than the usual 70 percent and since the partial pressure of product water was not reduced by utilization of recycle gas to the converter, the ratio of water to synthesis gas was high and the usage ratio low. It was thus indicated that more fresh gas would have to be injected into the converter to get higher space-time yields and usage ratios.

To provide the normal amount of fresh gas to the converter and at the same time utilize all gas (both fresh and recycle) in both the stripping column and the converter, conditions were established to simulate those that would exist if the stripping column were operated in series with the converter. In series arrangement (fig. 18), fresh and recycle gas passed first to the stripping column, and that portion of the gas that was not absorbed in the circulating oil passed into the bottom of the converter after condensation of most of the water.

To avoid extensive modification to the pilot plant that would have been necessary to operate in series, the converter and stripping column were connected and operated in parallel in the manner described previously (see fig. 16, p. 46). The only essential difference between the 2

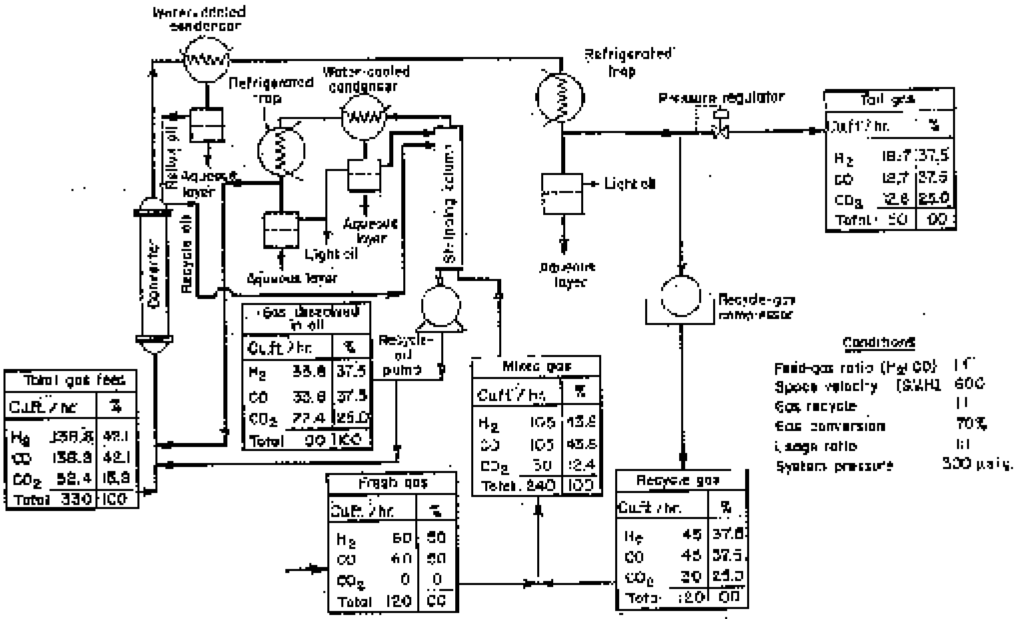

FIGURE 18.—Simulated Operation With Stripping Column in Series With Internally Cooled Converter.

schemes is that the gas passing through the stripping column in parallel operation contained 25 volume-percent of carbon dioxide, while in series operation it would have contained 12.4 volume-percent. (All gas analyses are on a hydrocarbon- and water-free basis.) For a basis of comparison a short period of normal operation (without the stripping column) was also conducted at the same fresh gas rate, recycle ratio, pressure, and gas conversion. Data for both periods are given in table 27. The maximum temperature required with the stripping column in service was 4° C. less than that for normal operation. The usage ratio served as the criterion for determining the effectiveness of operation with the column. Significantly, for operation with the stripping column in service, the average usage ratio was 1.0 (actually it ranged between 0.97 and 1.03), compared with only 0.87 without the column. For operation without the column a recycle ratio of about 2 would probably have been needed to attain a usage ratio of 1. Thus, only half of the volume of recycle gas was needed when the stripping column was used. On the basis of this improvement it seems reasonable to assume that a satisfactory usage ratio, that is, one equal to or approaching the feed-gas ratio, could be achieved with a $1.3H_2$: 1CO gas without excessive gas recycling. As discussed previously, this is of utmost importance in a two-stage process where the exit gas from the first stage is used as the feed gas to the second. Probably as a result of the stripping action of the gases on the oil stream, the acid number of the circulating oil averaged only 0.1 mg. of potassium hydroxide per gram of oil compared with values of 0.2 to 0.5 obtained during normal operation. No significant changes were observed in the product distribution.

TABLE 27.—*Comparison of synthesis conditions with and without stripping column in experiment 23–B*

	Without stripping column	With stripping column
Duration hr.	24	264
Synthesis gas:		
Ratio in fresh gas, H_2:CO	1.0	1.0
S. V. H. (settled bed)	600	600
Conversion, vol.-percent H_2+CO	68.4	70.0
Usage ratio, H_2:CO	0.87	1.00
Gas-recycle ratio	1	1
Pressure:		
Maximum p. s. i. g.	298	297
Differential p. s. i.	4	3
Temperature, ° C.:		
Maximum	248	244
Differential	4	3

ACTIVATION TREATMENTS

To obtain greater stability and longer catalyst life, several methods of increasing the activity were tested during the expanded-bed experiments.

"Typhoon" Induction.—One treatment (experiments 21, 27, 28), patterned after Kölbel's "typhoon" induction (*44*), consisted of passing a hydrogen-rich synthesis gas at high linear velocity and low pressure (20 to 30 p. s. i. g.) over the reduced catalyst. It was carried out under the following conditions:

Fresh gas ratio, H_2:CO	3
Fresh feed rate……cu. ft. per hr. (S.T.P.)	20
Fresh feed space velocity……hr.$^{-1}$	150
Gas-recycle ratio	1
Converter pressure……p. s. i. g.	30

After the pressure and gas flows were established, the average temperature was increased from 60° to 255° C. over a period of 15 to 25 hours. This temperature was maintained for about 30 hours, until the carbon dioxide-free contraction became stabilized at 35 to 40 percent, at which time the pretreatment was terminated.

In the initial test (experiment 21) this induction was followed by the stepwise induction and synthesis with $1.3H_2+1CO$. Operating temperature was lowered 5° to 10° C. below the values usually required for 70-percent conversion. However, this gain was attributed to the use of smaller (20- to 42-mesh) catalyst particles rather than to the "typhoon" treatment.

In experiments 27 and 28 the "typhoon" treatment was followed by induction[10] with $1.3H_2+1CO$ and the subsequent synthesis run conducted with $0.7H_2+1CO$. In these experiments the operating temperature was 5° to 10° C. higher than required in experiments 24 and 25, in which the catalyst was precarbided, or in experiment 26, in which reduction and stepwise induction were used. As no advantage accompanied "typhoon" induction, the procedure was abandoned.

Garbiding.—Another departure from the usual preconditioning procedure was made in experiments 24 and 25, in which the freshly reduced iron was carbided at low pressure before stepwise induction and synthesis. Similarly treated catalysts were found to be quite stable over long periods when tested in small, dry-bed units at 100 p. s. i. g. pressure.

To carry out this procedure, a carbon monoxide-rich gas was passed over the reduced catalyst at 200° to 275° C. and 20 p. s. i. g. The treatment for experiment 24 required 92 hours; the carbiding agent was $0.25H_2+1CO$ passed over the catalyst at an hourly space velocity of 50. Similarly, in experiment 25 a gas having the ratio of $0.7H_2$:1CO was used at space velocities of 50 to 100; the time of treatment was extended to about 155 hours. In both cases gas recycle was employed at an hourly space velocity of 100. Carbon dioxide was removed from this stream to a concentration of less than 1 volume-percent; this limited the carbon dioxide concentration in tail gas to a maximum of 15.5 volume-percent. X-ray and magnetic analyses showed that about 85 to 90 percent of the iron had been converted to Hägg iron carbide; these values agreed with a carbon-iron atomic ratio of 0.453–0.467, determined from chemical analyses. Nearly all of the iron that was not carbided remained metallic; only a negligible amount of magnetite was formed.

After stepwise induction with $0.7H_2+1CO$, synthesis was conducted at a space velocity of 600, 300 p. s. i. g., and with a gas-recycle ratio of 1 (without carbon dioxide scrubbing). A relatively short time of synthesis showed that neither activity nor stability had been improved. During the first 7 days of operation, a temperature increase of 14° C. in experiment 24 and of 11° C. in experiment 25 was necessary to maintain the desired conversion. Only short periods of steady-state operation could be maintained (table 28), as the activity diminished rapidly. Both experiments were terminated after only 500 to 600 hours of operation.

TABLE 28.—*Data for steady operating conditions in experiments 24–A and 25–A*

Experiment No.	24–A	25–A
Catalyst, age for period……hr.	364–508	321–389
Synthesis gas:		
Ratio in fresh gas, H_2:CO	0.68	0.69
S. V. H. (settled bed)	597	598
Flow……cu. ft./hr. (S. T. P.)	109.8	110.0
Conversion……vol.-percent H_2+CO	65.3	58.1
Usage ratio, H_2:CO	0.67	0.70
Gas-recycle ratio	1	1
Maximum……p. s. i. g.	290	299
Differential……p. s. i.	4	3
Temperature, ° C.:		
Maximum	268	269
Differential	8	7
Yields, specific……gm. C_1+C_2 m.^{3}	26.8	24.8

Loss of activity in both experiments was accompanied by excessive disintegration of catalyst. During experiment 24 the iron content of the circulating oil rose to 3 to 4 percent compared with expected normal values of less than 0.1 percent. Inspection of the catalyst bed at the end of experiment 25 showed that only about 27 percent of it (by volume) was still in the converter, and this was much finer than the originally charged 6- to 20-mesh material.

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[10] This was not the stepwise induction. Instead, the temperature was increased gradually from 200° to 250° C. over a 30-hour period. When only 55-percent carbon dioxide-free contraction was obtained, the temperature was further increased to 257° C., and 58-percent gas conversion resulted. After 12 hours under these conditions, a switch was made to $0.7H_2+1CO$.

Extreme catalyst disintegration had also occurred during synthesis with $0.7H_2+1CO$ following carburization of a used catalyst (2,250 hours) in place under oil (experiment 22–D).

Experiments 24 and 25 are to be compared with experiment 26, in which the catalyst was inducted by the stepwise method. Synthesis conditions of pressure, flow, recycle and feed-gas composition were duplicated in all three tests, but throughout experiment 26 carbon dioxide was removed from the recycled gas. In contrast to the performance in experiments 24 and 25, experiment 26 was very productive and the catalyst durable.

Even though more satisfactory operation might have resulted had carbon dioxide been removed from the recycle gas in experiments 24 and 25, carbiding apparently is not a desirable procedure. Later studies in small, dry-bed units have shown that no advantages are gained by carbiding a reduced, fused catalyst if synthesis is to be conducted at 300 p. s. i. g. pressure.

Although the products from experiments 24 and 25 differed somewhat from those obtained in experiment 26, they displayed certain characteristics typical of operation with $0.7H_2+1CO$. Even though a relatively high temperature was employed (17° C. higher than that required in experiment 26), the specific yield of C_1 plus C_2 hydrocarbons was only about 26 gm. per $m.^3$ compared with 29.5 in experiment 26. Table 29 shows that the shift in product distribution toward higher molecular weight, characteristic for carbon monoxide-rich gas, was less pronounced with carbided catalyst, probably because of the higher operating temperature. At 268° C. and with $1H_2+1CO$ or $1.3H_2+1CO$, a gasoline yield of 65 to 75 percent (by weight) would be expected.

Both chemical and X-ray analyses of catalyst samples taken at the conclusion of experiments 24–A and 25–A (table 30) showed that after only 500 to 600 hours of synthesis considerable amounts of magnetite replaced the Hägg iron carbide. On the other hand, in experiment 26 A after 1,188 hours of synthesis about 55 percent of the iron was still present either as hexagonal, close-packed iron carbide or metallic iron (fig. 19). The superior activity and stability of the catalyst in experiment 26 might be ascribed to the slow rate of oxidation because carbon dioxide was removed from the recycle gas.

These observations are not intended to suggest a causal relationship between catalyst phases and activity. All that is known now, from numerous analyses of used catalysts, is that metallic iron is quickly carbided at the start of synthesis and that iron carbide is gradually replaced by magnetite as a test progresses. The activity usually decreases with time.

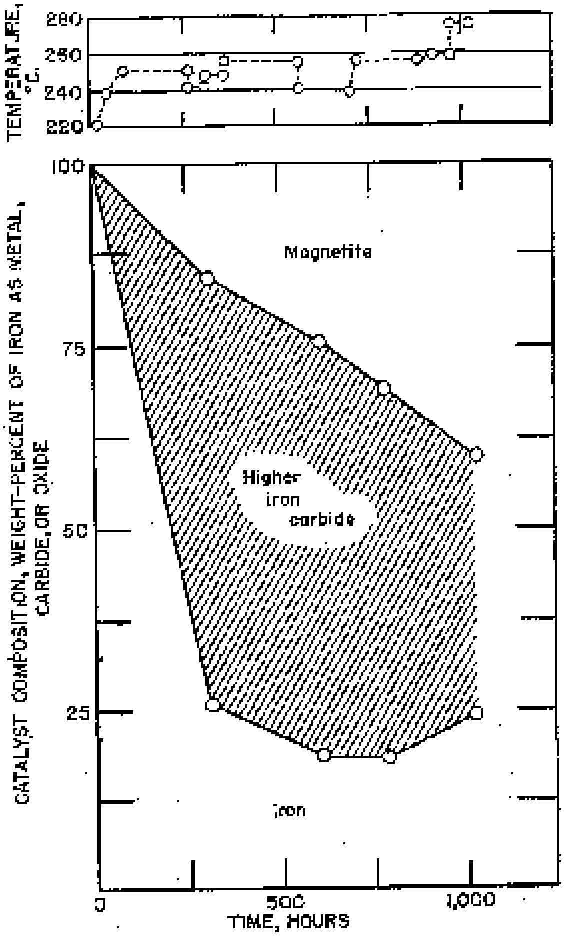

FIGURE 19.—Distribution of Iron in Catalyst D-3001 During Experiment 26–A.

TABLE 29.—*Comparison of distribution of C_4+ products from experiments 24–A[1] and 26–A[1]*

Experiment No.	24–A[2]		26–A[3]	
	Lb. per day[4]	Wt.-percent	Lb. per day[4]	Wt.-percent
Gasoline (C_4+)	9.84	58.3	9.24	52.9
Diesel oil	2.43	14.4	2.15	12.3
Heavy distillate	2.17	12.9	3.76	21.5
Wax	2.43	14.4	2.32	13.3
Total C_4+ production	16.87	100.0	17.47	100.0

[1] 600 S. V. H., $0.7H_2$:1CO, 70-percent conversion, 300 p. s. i. g.

[2] Maximum temperature, 268° C., without removal of carbon dioxide; bauxite unit not in service.

[3] Maximum temperature, 251° C., with removal of carbon dioxide; bauxite unit in service at 325° C.

[4] Includes oil-soluble oxygenates.

TABLE 30. *Analyses of discharged catalysts at the conclusion of experiments 24–A and 25–A*

(Weight-percent)

Experiment No.	24 A	25 A
Chemical analysis:		
Total Fe	70.37	68.01
Metallic Fe plus carbide (as Fe)	27.64	16.00
Total C	9.61	4.60
Acid-insoluble C	6.90	3.41
Reduction, percent	53.50	23.10
Calculated [1] composition:		
Fe_3O_4	45.0	73.2
Higher iron carbide (assumed Fe_2C)	27.0	14.7
Fe	28.3	12.1
X-ray analysis:		
Ferrous components in order of decreasing concentration	Fe_3O_4, Hägg carbide, α-Fe.	Fe_3O_4, α-Fe, perhaps Hägg carbide.
Fe_3O_4: α-Fe (approximately)	75:25	80:20

[1] From chemical analysis.

EFFECT OF RECYCLE RATIO ON YIELDS OF C_1 PLUS C_2 HYDROCARBONS AND ON USAGE RATIO

A series of tests (table 31 and fig. 20) was carried out during experiment 19–E to determine the effect of recycling gas on the yield of C_1 plus C_2 hydrocarbons and on the H_2:CO usage ratio. In these tests, the hourly space velocity of fresh synthesis gas ($1.3H_2$+1CO) was 230, based on the volume of the expanded bed (300 based on the volume of the settled bed). A 70-percent conversion was maintained by adjusting the temperature; and the gas-recycle ratio was increased in steps from 1 to 6 and then returned to 1 to make sure that no changes had occurred in the behavior of the catalyst. Table 31 and figure 20 show that, at a recycle ratio of 6, the usage ratio was highest and the yield of C_1 plus C_2 hydrocarbons lowest. Both results are favorable to efficient conversion of the synthesis gas. However, these advantages might be offset by the increased cost of recycling.

USE OF BAUXITE REACTOR DURING SYNTHESIS

In several expanded-bed experiments oxygenated compounds in the primary "overhead" products were decomposed to hydrocarbons by passing the vapors through a bed of alumina (bauxite). Removal of these compounds in the

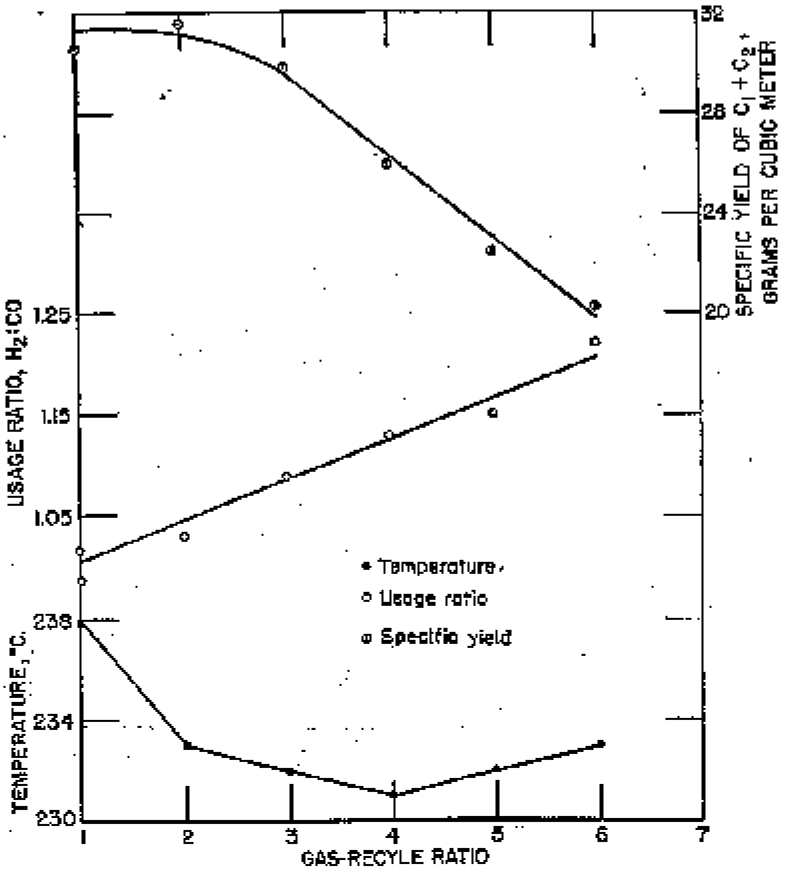

FIGURE 20.—Effect of Gas-Recycle Ratio on Specified Yield of C_1+C_2 and Usage Ratio at 70-Percent Conversion in Experiment 19.

converter system should simplify refining of the product; reduce the amount of organic acids in the reactor; minimize the problem of disposal of the aqueous product; and simplify removal of carbon dioxide from the recycle gas by amine, with which organic acids form stable complexes. In addition, this treatment should result in upgrading of the primary naphtha product. Beneficial results from catalytic re-forming of a synthetic Fischer-Tropsch naphtha were obtained by Helmers, Clark, and Alden (*25*). Bauxite destroys oxygenated compounds by dehydration, decarboxylation, and decarbonylation. Conversion of α- to δ-olefins and isomerization of straight- to branched-chain olefins also occur, both of which improve the octane rating of the naphtha.

TABLE 31.—*Effect of gas-recycle ratio on specific yield of C_1+C_2 and usage ratio in experiment 19–E*

[Duration, 12 hr. Synthesis gas—ratio in fresh gas, H_2:CO, 1.3. S. V., H. (settled bed), 300; conversion, vol.-percent H_2+CO, 70; pressure, average, 300 p. s. i. g.]

Test No.	1	2	3	4	5	6	7
Synthesis gas:							
Usage ratio, H_2:CO	0.46	1.03	1.08	1.13	1.15	1.22	1.02
Gas-recycle ratio	1	2	3	4	5	6	1
Temperature, average, °C.	235	233	232	231	232	234	236
Yields, specific, gm. C_1+ C_2 per m.³	33.7	31.6	30.2	28.0	22.5	26.3	30.6

To take advantage of the elevated temperatures and pressures in the system the vapors from the converter were preheated and passed through the bauxite before they entered the condensing system. The bauxite reactor was a 2-foot length of 4-inch-diameter pipe, charged with 0.133 cu. ft. of catalyst. The total hourly flow through the reactor was about 180 cu. ft. and consisted of tail and recycle gas, slightly over 1 gallon of hydrocarbons (reflux and light product oil), and 0.25 to 0.5 pound of water. The rate of production of light oil, including C_3 to C_6, was only about 0.07 gal. per hr., so that most of treated hydrocarbons were refluxed to the converter.

Two types of bauxite were tested in experiments 22 and 26: 4- to 8-mesh activated alumina "F–1", obtained from the Aluminum Co. of America, and 4- to 12-mesh "Phillips Cyclocel," obtained from the Phillips Petroleum Co. Both reduced oxygenated compounds by about 90 percent in the oil and 60 percent in the aqueous layer, so that about 60 percent of the total oxygenates was destroyed. Cyclocel seemed more active at low temperatures and was about as effective at 325° C. as F–1 at 370° C.; in addition, it was more effective for shifting double bonds to internal positions in the gasoline fraction. Gasoline, as produced in experiment 26 in which Cyclocel was used, had a motor octane rating of about 68, or 16 to 17

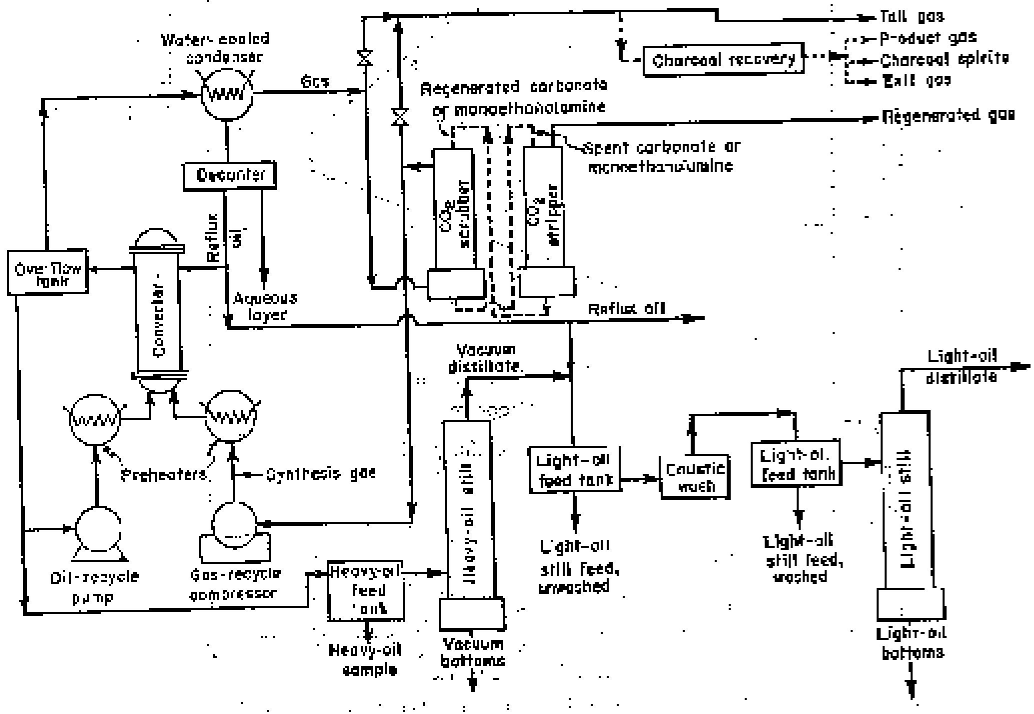

FIGURE 21.—Submerged-Bed, Barrel-per-Day Unit, Pilot Plant 3.

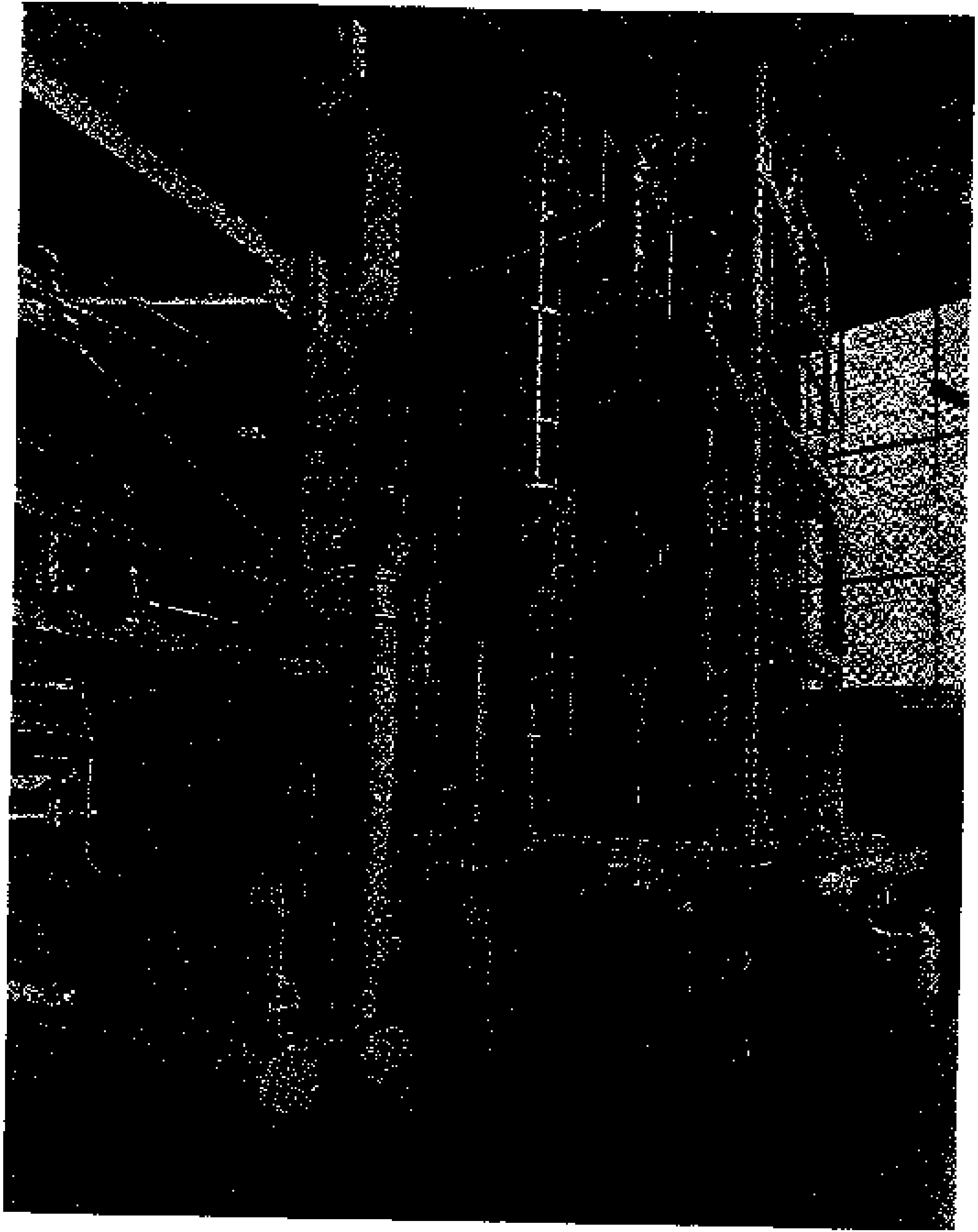

Figure 22.—Pilot Plant 3, Barrel-per-Day Capacity.

points higher than untreated gasoline. An increase in the yield of C_1 plus C_2 gas of about 5 gm. per $m.^3$ appeared to accompany the bauxite treatment.

EIGHT-INCH-DIAMETER REACTOR (BARREL-PER-DAY PLANT), WITH EXPANDED BED

OBJECTIVE

A moderately large pilot plant having a reactor 8 inches in diameter with a production capacity of approximately 1 barrel per day of total liquid product (C_3+ hydrocarbons) was placed in operation on completion of experiment 29. This plant operated on the expanded-catalyst-bed principle and incorporated the procedures and improvements developed in experiments 18 to 29.

The purpose of this operation was to learn whether the results of the small pilot plants could be duplicated and whether new problems would be encountered in a larger reactor. Two experiments were conducted, one with $0.7H_2+1CO$ and the other with $1H_2+1CO$. The increase in scale was fourteen-fold in going to an 8-inch-diameter reactor (unit 3) from the 3-inch units (Nos. 1 and 2) and to a bed of settled catalyst 8 feet high from a bed 4 feet high. The increased production provided enough material for more complete characterization and furnished samples of diesel and jet fuels to the Army and Navy.

APPARATUS

Except for its increased size and the addition of continuous distillation units, the larger pilot plant was basically the same as the smaller units but included more complete instrumentation to provide for automatic control of temperature, pressure, and flow where practical.

Figure 21 shows schematically the more important parts of the system and the flow of the gas and oil streams; figure 22 is a photograph of the plant. Some of the details of the reactor such as locations of entries, catalyst-sampling points, and thermocouples are illustrated in figure 23. Because the supply of synthesis gas was limited, only an 8-foot settled height of catalyst was charged. Mixed gas, consisting of fresh and recycle gases, entered the bottom of the reactor with the recycle oil, which flowed at a linear velocity of 0.15 to 0.25 ft. per sec. based on the free cross-sectional area of the reactor. Both streams were heated in fin-tube heat exchangers by condensation of Dowtherm vapor supplied by a small boiler operated at 50 p. s. i. g. Gas and oil flowed upward, expanding the catalyst bed. Reaction products, unreacted gases, and circulating oil were conducted out the top of the converter and through a 2.5-inch pipe to an overflow tank. Recycle oil flowed by gravity from the bottom of this tank to the inlet side of a centrifugal pump for recirculation, and the gases and vapors passed overhead to the condenser system. Heavy reaction products were continuously withdrawn by maintaining a constant level in the converter with an automatic liquid-level controller. This heavy material was separated into 2 fractions in a vacuum still, maintained at an absolute pressure of about 40 mm. mercury; the cut point was equivalent to about 316° C. at atmospheric pressure. The distillate, consisting of gasoline and diesel oil, was washed with aqueous caustic solution to remove organic acids, and the gasoline was separated by distillation at atmospheric pressure to 204° C.

Gases and vapors from the overhead tank were cooled to about 25° C. in the condensing system, and the condensate was sent to a decanter in which the aqueous and oil layers were continuously separated and withdrawn. The aqueous layer was discharged and collected, and the oil could either be refluxed to the converter to prevent a buildup of the wax content or discharged as product. Discharged reflux oil was combined with the distillate from the vacuum still. The reflux rate varied between 10 and 30 gal. per hr. Part of the effluent gas from the condenser was recycled, generally after removal of carbon dioxide; the remainder was let down to atmospheric pressure and left the system as tail gas. When mass balances were desired, a portion of the tail gas was passed through activated charcoal, where C_3 and heavier hydrocarbons were adsorbed.

The scrubbing system for removing carbon dioxide was of conventional design with fresh (regenerated) aqueous potassium carbonate or monoethanolamine (M. E. A.) fed into the top of the absorber through a distributor, and gas flowing countercurrently. The absorber column was a 6-inch pipe, packed to a height of 8 feet with ⅜-inch ceramic Raschig rings. The stripper column was also a 6-inch pipe, packed to a height of 6 feet with ⅜-inch ceramic Raschig rings. Initially (experiment 30) a 12- to 15-percent carbonate solution was used; but, because flooding was encountered in the stripper at flow rates of only about 1.25 gal. per min., the amount of carbon dioxide in the recycle gas was not reduced sufficiently. When the carbonate was replaced by 20-percent M. E. A. the rate of flow was increased to 2.2 gal. per min., and the amount of carbon dioxide