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 10 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 1.26 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

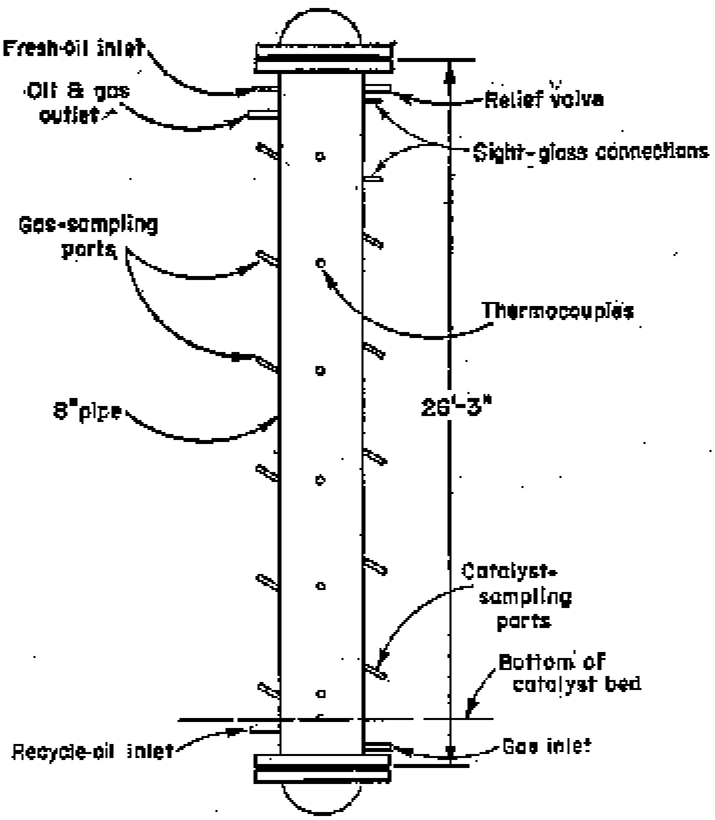

Figure 23.—Barrel-per-Day Converter.

in the scrubbed gas was lowered to less than 2 percent. The scrubbed gas was recycled, and the spent solution was heated and regenerated in a stripper column. The stripped gas consisted of about 95 percent carbon dioxide and small quantities of synthesis gas and hydrocarbons.

RAW MATERIALS

SYNTHESIS GAS

During the first part of experiment 30, $0.7H_2+1CO$ was used as the feed gas. At 70-percent conversion with a gas-recycle ratio of 1, unusually high usage ratios were experienced that could not be corrected by varying the recycling rate. The composition of the gas was therefore changed to $1H_2+1CO$ for the latter part of the experiment (30–C) and at the start of the next experiment (No. 31). Preparation and specification of the gases have been described under Bench-Scale, Trickle-Flow Investigations (see p. 9).

CATALYST

About 2.6 cu. ft. (306 pounds) of reduced catalyst was needed for a charge. To prepare each charge 2 batches of raw 6- to 20-mesh catalyst D–3001, each weighing approximately 200 pounds, were reduced with hydrogen in a plant constructed for this purpose. A simplified flow diagram of this plant is shown in figure 24. The reductor was constructed of 12-inch-diameter, Schedule-40 pipe and had a charging volume of 2.1 cu. ft. when filled to a maximum height of 32 inches.

In general, the reduction procedure paralleled that used in experiments 21 to 29 in the smaller reduction plant. (See Expanded-Bed Experiments, Catalyst, p. 33.) Fresh and recycle hydrogen was passed over the catalyst at an hourly space velocity of 2,000 and atmospheric pressure for 120 hours, while the temperature was gradually increased from 300° to 500° C. to keep the concentration of water vapor in the exit gas below 7.0 gm. per $m.^3$ Silica-gel driers reduced the concentration of water vapor in the inlet gas to less than 0.035 gm. per $m.^3$ A reduction of 95 percent or more was achieved. To prevent oxidation the reduced catalyst was stored under a neutral oil until needed for charging the converter.

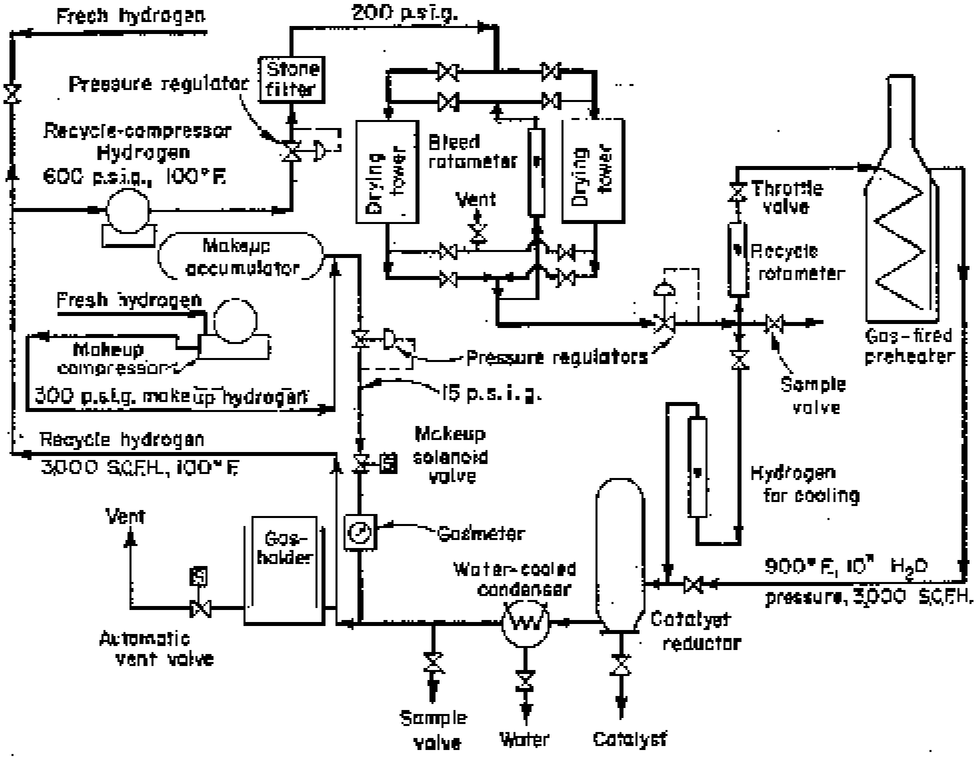

FIGURE 24.—Catalyst Reduction Unit for Barrel-per-Day Plant.

COOLING OIL

For initial operation in experiment 30, a low-boiling diesel from Harnes (boiling $<250°$ C.) was used as cooling oil. As the experiment progressed, this oil was replaced by oil produced in the synthesis. Before the oil was fed to the converter, it was washed with caustic and water to remove acidic material. During synthesis the linear velocity of oil was maintained at 0.15 to 0.25 foot per second to obtain satisfactory expansion of the bed and also to hold the temperature differential along the bed between 4° and 8° C. (usually 4° to 5° C.). The level of the catalyst was indicated by a weighted float-and-pointer similar to that used in the small plants.

OPERATIONS

$0.7H_2+1CO$ FEED

Because $0.7H_2+1CO$ was believed to be cheaper than $1H_2+1CO$ made from coal, and, following a satisfactory test (experiment 26) with this gas in a small unit, synthesis was started with $0.7H_2+1CO$.

After reduction and stepwise induction of the catalyst at an hourly space velocity of 600, 450 p. s. i. g. pressure, with a gas-recycle ratio of 1, with removal of carbon dioxide, 70-percent conversion of gas was attained under the conditions given in table 32.

The activity was not as high as that in experiments 26–A (normally reduced) and 27–A ("typhoon" inducted) in which 70 percent of the $0.7H_2+1CO$ feed gas had been converted at 238° to 242° and 246° C., respectively, at 400 p. s. i. g. pressure. However, the amount of carbon dioxide in the recycle gas of experiment 30–A was about 10 percent, whereas in experiments 26–A and 27–A it had been only about 2 to 3 percent. This increase occurred because a high enough rate of circulation of absorbent solution could not be maintained in the absorber without the danger of flooding. The specific yield of 29.2 gm. per $m.^3$ of C_1 plus C_2 hydrocarbons was 5 to 10 gm. higher than in experiments 26–A and 27–A. As a result of inefficient removal of carbon dioxide from the recycle gas, the activity fell rapidly, and this part of the experiment (30–A) was terminated after only 327 hours of synthesis.

Without withdrawing the coolant, the catalyst was given an activation treatment with hydrogen at a low temperature (250° C.), after which

TABLE 32.—*Initial operating conditions at 65-percent carbon dioxide-free contraction in experiment 30–A*

Synthesis gas:	
Ratio in fresh gas, H_2:CO	0.7
S. V. H. (settled bed)	599
Flow, cu. ft. per hr. (S. T. P.)	1583
Conversion, vol.-percent H_2+CO	71.1
Usage ratio, H_2:CO	0.72
Gas-recycle [1] ratio	1
Pressure:	
Maximum, p. s. i. g.	453
Differential, p. s. i.	5
Temperature, °C.:	
Maximum	254
Differential	8
Yields, specific, gm. C_1+C_2 per m.³	29.2

[1] Carbon dioxide content of recycle gas was approximately 10 volume-percent.

70-percent gas conversion was attained at 251° to 253°, in experiment 30–B. The amount of carbon dioxide in the recycle gas during this period was reduced to between 2 and 3 percent by using 20-percent M. E. A. instead of the carbonate. Unusually high usage ratios, ranging from 0.78 to 1.01, were realized. This was the first time the usage ratio exceeded that of the feed gas to such an extent.

Because of the high content of carbon monoxide in the recycle gas, a relatively small specific yield of C_1 plus C_2 was obtained. However, the over-all hydrocarbon distribution was unfavorable, as a relatively large amount of wax and little gasoline were being produced. Table 33 presents data from this experiment, with results of experiment 26. The slightly higher pressure employed in experiment 30 probably had little influence on the product distribution.

The high specific yield of C_3+ hydrocarbons—188.1 gm. per m.³—for this period agreed closely with the theoretical yield (187.8 gm. per m.³), calculated from a balanced equation representing the synthesis reaction. In experiments in the smaller plants the discrepancy between actual and theoretical specific yields generally was about 10 to 20 gm., probably because of the smaller quantities of materials involved. The high yield was substantiated by a calculated mass balance of nearly 100 percent for carbon, hydrogen, and oxygen.

As the usage ratio increased from 0.78 to 0.89, the amount of iron in the oil rose sharply in 8 days from 0.24 percent to 4.25. Considerable amounts of fines were removed from the filters in the recycle-oil line, further indicating that disintegration of the catalyst was occurring. X-ray diffraction and magnetic analyses (table 34) of a sample of the black, insoluble material that was separated from the circulating oil by repeated extractions with hot toluene showed that, on a hydrocarbon-free basis, this material was predominantly Hägg iron carbide with some magnetite. The occurrence of very fine particles of iron carbide in the oil may be attributed to the effect of the higher partial pressure of carbon monoxide or lower H_2:CO ratios that prevailed at the high usage ratios (fig. 25).

When it was established that the usage ratio could not be corrected by variation of the recycle ratio between 0.5 and 2 and the catalyst continued to deteriorate in activity and to disintegrate, experiment 30–B was terminated. The catalyst was given another activation treatment with hydrogen, and experiment 30–C was begun with $1H_2+1CO$ feed gas. Operation with this gas was maintained for a short period only, but the results indicated that a normal usage ratio of 0.92 and satisfactory yield of C_1 plus

TABLE 33.—*Comparison of operating conditions and distribution of C_3+ products for experiments 26–A and 30–B*

[Synthesis gas—ratio in fresh gas, H_2:CO, 0.7; S. V. H. (settled bed), 600. Gas-recycle ratio, 1]

Experiment No.	30–B	26–A	26–A
Pilot plant No.	3	2	2
Catalyst age for period, hr.	408–510	552–648	324–364
Cyclical reactor temperature, °C.	(1)	[2] 325	325
Synthesis gas:			
Flow, cu. ft. per hr. (S. T. P.)	1580	110.3	110.2
CO_2-free contraction, vol.-percent	65.8	55.3	52.5
Conversion, vol.-percent:			
CO	65.0	67.3	58.9
H_2	74.7	49.6	60.6
H_2+CO	69.0	58.3	58.7
Usage ratio, H_2:CO	0.83	0.70	0.60
Recycle gas:			
CO_2 content, vol.-percent	2.7	2.4	4.8
Pressure, average, p. s. i. g.	440	404	405
Temperature, °C.:			
Maximum	251	253	265
Differential	5	4	5
Yields, specific, gm. per m.³:			
CH_4	8.0	10.8	14.5
C_2H_4	6.2	0.0	12.8
C_2H_6	5.4	3.6	2.8
C_3H_6	3.6	8.2	7.4
C_3H_8	14.8	4.7	14.1
C_4H_8	3.0	9.4	3.9
C_4H_{10}	10.1	11.0	12.2
C_5H_{10}	0.7	2.4	1.6
C_5H_{12}	5.9	11.6	7.8
C_6H_{12}	0.4		
C_6H_{14}	3.8	7.5	2.7
C_7+	1.0		
C_3+, actual	188.1	172.0	159.7
Products:			
Recovery, lb. per day:			
Heavy oil	187.47	11.53	11.55
Light oil	25.60	1.78	3.25
Reflux oil		0.83	0.95
Charcoal spirits and gas	[3] 69.94	(4)	(4)
Aqueous layer	114.27	0.36	6.42
Distribution of C_5+, lb. per day: [5]			
Gasoline (C_5+)	152.88	9.30	12.74
Diesel oil	50.16	2.58	3.56
Heavy distillate	44.89	4.64	3.87
Wax	75.96	3.25	2.71
Distribution of C_5+, wt.-percent: [5]			
Gasoline (C_5+)	41.7	42.6	55.7
Diesel oil	17.0	13.7	15.6
Heavy distillate	15.3	21.8	16.9
Wax	25.0	19.1	11.8

[1] Reactor out of service.
[2] Reactor in intermittent service.
[3] Includes C_3–C_4 components in the exit and regenerated gases.
[4] No charcoal recovery.
[5] Includes oil-soluble oxygenates.

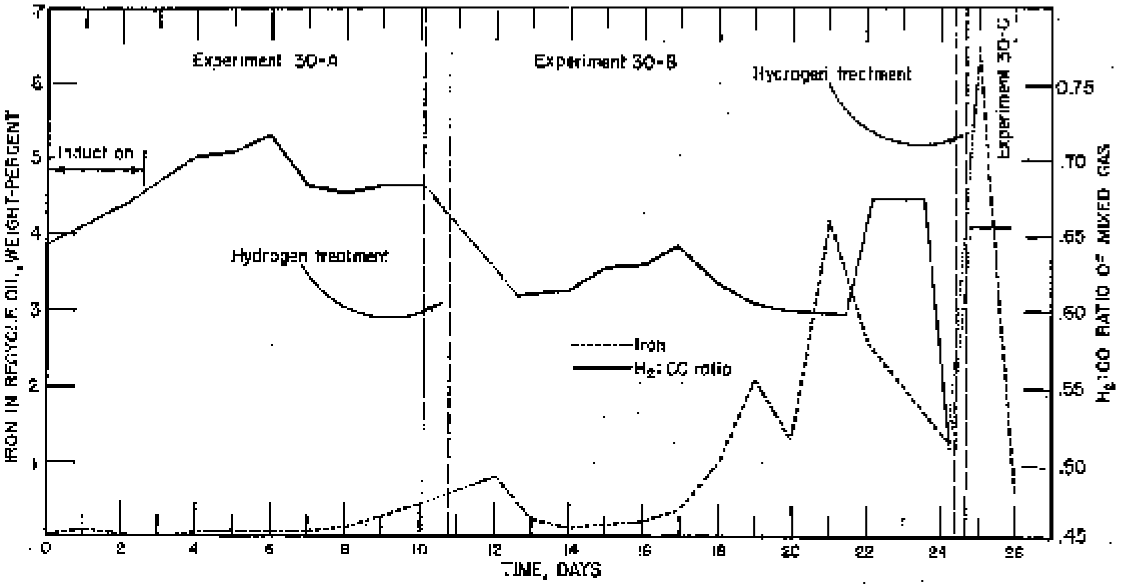

Figure 25.—Effect of Mixed-Gas Ratio on Iron Content of Recycle Oil in Experiment 30.

C_2 hydrocarbons could be attained. Synthesis was terminated after a total of 677 hours.

$1H_2+1CO$ FEED

Experiment 31 was begun with a fresh charge of catalyst D-3001 and $1H_2+1CO$ feed gas. After normal, stepwise induction at an hourly space velocity of 600, 400 p. s. i. g., and with a 1:1 gas-recycle ratio (carbon dioxide removed from the recycle gas), 70-percent conversion was attained at 235° C. A temperature of 254° C. had been required for the same conversion initially in experiment 30–A with $0.7H_2+1CO$.

Table 34.—*Analyses of material separated*[1] *from recycle oil of experiment 30–B*

(Weight-percent)

Chemical analysis, total Fe	24.6
X-ray and magnetic analyses, total Fe as—	
Fe_2C (Hägg)	[2] 73.9
Fe_3O_4	26.1

[1] By extraction with toluene.
[2] Paraffin also present, in addition to magnetic components.

Although the desired usage ratio was attained subsequently at gas-recycle ratios between 1 and 1.25, a more rapid loss of conversion was observed than had occurred in the small plants, and frequent increases in operating temperature were necessary. Three hydrogen treatments of the submerged catalyst were required during only 868 hours of operation. Again, unusually high concentrations of iron appeared in the recycle oil, and considerable amounts of fines were removed from the filters in the recycle-oil line. X-ray and magnetic analyses (table 35) showed, as previously, that this material was chiefly Hägg carbide. The presence of ferrous carbonate was also indicated by the X-ray diffraction patterns. In both experiments 30 and 31 the catalyst remaining in the converter at the end of the run was very similar in particle size to that originally charged. Thus, complete disintegration of selected particles, rather than partial attrition of all particles, appeared to occur.

Table 35.—*Analyses of material separated*[1] *from recycle oil of experiment 31–C*

(Weight-percent)

Chemical analysis:	
Total Fe	25.63
Total C	58.57
H_2	9.17
CO_2	9.4
Magnetic analysis, total Fe as—	
Fe_2C (Hägg)	65
Fe_3O_4	35
X-ray analysis:[2]	
$FeCO_3$	
Fe_2C (Hägg)	
Paraffin	
Fe_3O_4	

[1] By extraction with toluene.
[2] Shown in order of decreasing concentration.

Two periods were selected from experiment 31–C in which the data were considered representative of the operation. A summary of the operating conditions, product recoveries, calculated yields, and the product distributions during these periods is given in table 36, which also includes comparable data from experiments 22–B and 30–B. Although the operating temperature in experiment 31–C was 15° to

20° C. higher than in experiment 22–B; the C_3+ hydrocarbon distribution was similar. The yield of C_1 plus C_2 compounds was somewhat higher (3 to 7 gm. per $m.^3$) for experiment 22–B, probably because the bauxite reactor had been operated during the selected period.

The yields from both the barrel-per-day plant and the small pilot plants varied with the composition of the synthesis gas in the same manner. More gasoline and less wax were produced with $1H_2+1CO$ than with carbon monoxide-rich gas; the yields of diesel oil and heavy distillate did not change significantly. Possibly because of the higher partial pressure of hydrogen in the feed gas in experiment 31–C, the specific yield of C_1 plus C_2 hydrocarbons was higher by about 5 to 10 gm. per $m.^3$ than in experiment 30–B; for the same reason the degree of saturation of

TABLE 36.—*Comparison of operating conditions and distribution of C_3+ products for experiments 22–B, 30–B, and 31–C*

[Synthesis gas, S. V. H. (settled bed), 800]

Experiment No.	22–B	30–B	31–C	31–C
Pilot plant No.	2	3	3	3
Catalyst age for period, hr.	475–506	438–510	408–624	606–864
Bauxite reactor temperature, °C.	370	(1)	(1)	(1)
Synthesis gas:				
Ratio in fresh gas, H_2:CO	1.0	0.7	1.0	1.0
S. V. H. (settled bed)				
Flow, cu. ft. per hr. (S. T. P.)	110.4	1,535	1,536	1,554
CO_2-free contraction, vol.-percent	62.0	65.8	65.2	64.9
Conversion, vol.-percent:				
CO	65.5	65.0	71.5	71.2
H_2	66.1	74.7	66.5	65.4
H_2+CO	65.8	69.0	69.0	68.3
Usage ratio, H_2:CO	1.03	0.83	0.83	0.91
Recycle gas:				
Ratio	[2] 1	[3] 1	[3] 1.25	[3] 1.25
CO_2 content, vol.-percent	22.0	2.2	2.0	2.0
Pressure, average, p. s. i. g.	400	450	400	400
Temperature, °C.:				
Maximum	230	251	251–258	251–260
Differential	5	5	4	4
Yields, specific, gm. per $m.^3$:				
CH_4	10.0	8.6	14.8	11.1
C_2H_4	8.5	6.2	9.9	10.6
C_2H_6	5.2	5.4	4.9	4.2
C_3H_6	5.7	3.8	5.4	5.4
C_3H_8	7.9	14.8	19.1	19.2
C_4H_8	5.5	3.0	4.1	6.1
C_4H_{10}	13.8	10.1	11.4	11.5
C_5H_{10}	2.2	0.7	1.5	1.4
C_5H_{12}	10.8	6.9	5.2	6.0
C_6H_{12}	3.2	0.4	0.4	0.4
C_6H_{14}		3.8	2.3	2.3
C_7+		1.0	1.4	1.4
C_3+, actual	138.1	153.1	160.9	168.5
Products:				
Recovery, lb. per day:				
Heavy oil	5.65	187.5	34.6	44.6
Light oil	1.50	29.5	144.6	139.2
Reflux oil	1.74	0.0	0.0	0.0
Charcoal spirits and gas	(4)	[5] 59.8	[5] 80.5	[5] 86.3
Aqueous layer	11.61	114.8	115.9	144.6
Distribution of C_3+, lb. per day:[6]				
Gasoline (C_3+)	8.10	122.98	164.26	168.99
Diesel oil	1.89	50.16	36.75	38.04
Heavy distillate	2.20	44.99	29.13	28.87
Wax	2.32	76.86	28.99	35.67
Distribution of C_3+, wt.-percent:[6]				
Gasoline (C_3+)	57.5	41.7	64.6	62.4
Diesel oil	13.2	17.0	14.0	13.9
Heavy distillate	15.5	15.3	11.1	10.6
Wax	13.8	26.0	10.3	13.1

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[1] Reactor out of service.
[2] Without removal of carbon dioxide.
[3] With removal of carbon dioxide.
[4] No charcoal recovery.
[5] Includes C_1–C_5 components in the exit and regenerated gases.
[6] Includes oil-soluble oxygenates.

the C_3 to C_6 gases was higher for experiment 31–C. Actual specific yields of C_3+ hydrocarbons (160.9 and 168.5 gm. per m.³ in 2 instances) from experiment 31 were 14 to 18 grams lower than the theoretical yield. These discrepancies may be attributed in part to incomplete recoveries, as is evident from the fact that the mass balances for carbon, hydrogen, and oxygen were only 92 to 96 atom-percent. The specific yields of oxygenates (17 to 20 gm. per m.³) were 10 to 13 gm. per m.³ higher than the yields in experiment 30 and about 10 gm. per m.³ higher than normal. (See Products From Expanded-Bed Experiments; Oxygenated Compound p. 64) This difference has not been explained.

DISCUSSION

The barrel-per-day pilot plant was operated at an hourly space velocity of 600, with the gas conversion maintained at 70 percent, while the catalyst was active. Temperature control by nonevaporative cooling was precise and was independent of operating scale. There was complete freedom from catalyst cementation.

The plant performed better in some respects with $1H_2+1CO$ feed gas (experiment 31) than with $0.7H_2+1CO$ (experiment 30). In experiment 31 the usage ratio was maintained at a value substantially equivalent to the composition of the feed gas by means of gas recycle (ratio between 1 and 1.25). With the carbon monoxide-rich gas (experiment 30), however, the usage ratio (as high as 0.89) exceeded that of the feed gas and could not be corrected by varying the gas-recycle ratio between 0.5 and 2. A more desirable distribution of liquids was noted for $1H_2+1CO$ feed gas, more gasoline and less wax being produced. This effect of gas composition on product distribution is similar to that obtained in the small pilot plants. Ample quantities of products were collected for characterization, and a drum of caustic- and water-washed diesel oil from experiment 31 was sent to the United States Navy for field tests.

The rapid deterioration of the fused catalyst experienced in both experiments 30 and 31 was not anticipated and cannot be explained with absolute certainty. However, there are several possible causes. As has been previously discussed, the concentration of iron in the recycle oil and thus the rate of disintegration of the catalyst was higher when the partial pressure of carbon monoxide in the reactor was high. On the basis of this evidence, the partial pressures of carbon monoxide, carbon dioxide, hydrogen, and water in the reactor were determined for experiments 19, 22, 26, 27, 30, and 31 that are representative of operation with feed gases ranging from $0.7H_2+1CO$ to $1.3H_2+1CO$, with reduced fused-iron catalysts. These data were plotted against catalyst life in figure 26. Catalyst life varied considerably and only with the partial pressure of carbon monoxide; the partial pressure of each of the other gases was relatively constant. Within the range of carbon monoxide partial pressures (80 to 200 p. s. i. a.) an almost linear relationship existed between the durability of the catalyst and the pressure of carbon monoxide—the life of the catalyst was short at the high pressures of carbon monoxide. In experiments 24 and 25, not included in this study because the reduced catalysts were precarbided, rapid disintegration of the catalyst was also experienced with carbon monoxide-rich feed gas. It might be postulated that the high-carbon monoxide partial pressure favors carbon formation, which, in turn, is responsible for spalling of the catalyst.

Since a deeper bed of catalyst was employed in the barrel-per-day reactor than in the 3-inch-diameter converters, the linear velocities of both gas and coolant oil in the larger unit were greater for the same hourly space velocity of feed gas (600) and the same temperature differential (4° to 5° C.). Increased agitation of the catalyst bed at the higher velocities thus may also have contributed to rapid breakup of the catalyst.

Severe disintegration of catalyst in the barrel-per-day unit probably could have been avoided by improved operating technique and reduction of the carbon monoxide partial pressure in the reactor. However, because synthesis gas and manpower requirements for this unit made it necessary to curtail the operation of the other pilot plants, operation of the barrel-per-day plant was limited to the two experiments discussed.

PRODUCTS FROM EXPANDED-BED EXPERIMENTS

SCOPE

In this section the chemical and physical characteristics of the products obtained in the expanded-bed tests are given. Moreover, a method of treatment is described to transform the raw products into fuels comparable to those in commercial use. The raw product streams and their recovery are described, and a scheme is outlined for separating the crude product into the various commercial fractions.

Analyses of raw and treated gasolines are shown for experiments in which feed gases of various $H_2:CO$ ratios were used. Octane ratings of the raw and treated gasolines are given, and a brief comparison is made with synthesis products from a fluidized process. Physical

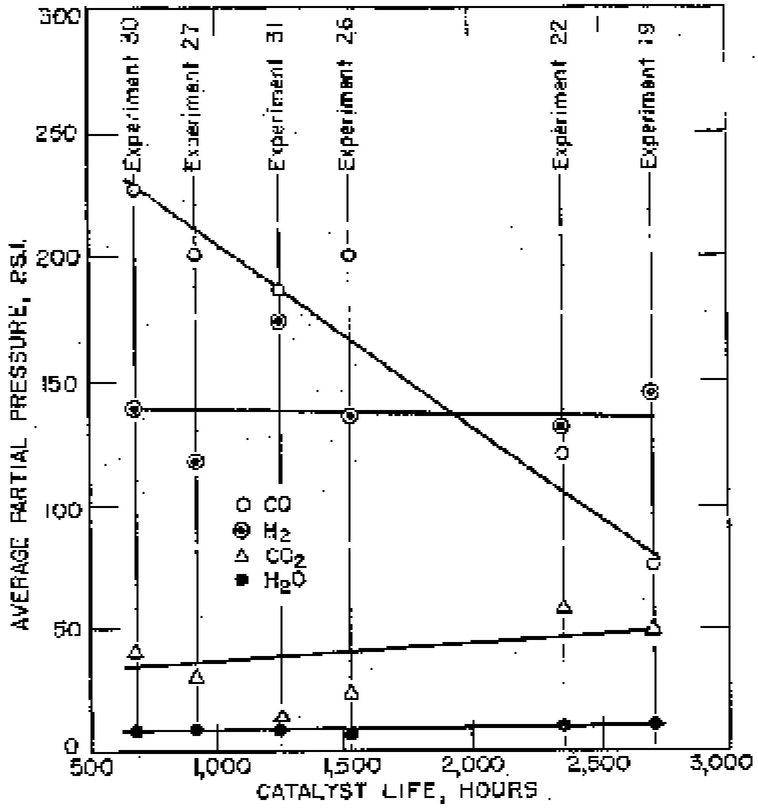

FIGURE 26.—Effect of Partial Pressure of Gases on Life of Catalyst.

properties of the material boiling above the gasoline range after separation into diesel, heavy distillate, and wax fractions are described.

Since the oxygenated compounds produced in the synthesis may be of interest, analyses are presented that show the nature and quantity of this material in both oil and aqueous phases. More detailed information was obtainable from the aqueous phase because quantitative analyses of specific compounds could be made by the mass spectrometer. Infrared analyses were used to determine the amounts of the various oxygenated groups in the oil fractions.

The effect of the operating variables upon the distribution of products as gasoline, diesel oil, and heavier products is discussed.

HYDROCARBONS

SEPARATION

Characterization data were obtained for the gasoline, diesel, heavy distillate, and wax fractions from synthesis with $1.3H_2+1CO$, $1H_2+1CO$, and $0.7H_2+1CO$ feed gases during experiments 21, 26, and 31. The general scheme for separation is outlined in figure 27. Four streams of raw product (recycle oil, light oil, reflux oil, and charcoal spirits) were collected for primary distillation. Recycle oil was withdrawn periodically from the circulating-oil line to maintain a constant level in the converter. Light oil was collected by cooling the overhead gases and vapors in a water-cooled condenser to about 45° C., then in a refrigerated trap to 5° C. The light oil was decanted from the water that condensed simultaneously. Reflux oil (that is, the high-boiling portion of the overhead stream) was returned to the converter. This oil was not intended to be a product, but as the size of the daily sample taken for analysis was an appreciable part of the total production in the smaller plants, it had to be included in the total product. It was not included with the products of the barrel-per-day unit. Part of the hydrocarbons, which had not condensed on cooling, was adsorbed in the charcoal. Condensables were recovered as charcoal spirits by steam stripping and cooling the evolved gases to about 10° C. The liquid-spirits portion was either added to the gasoline fraction (separated in the primary distillation) or to the original light oil before distillation.

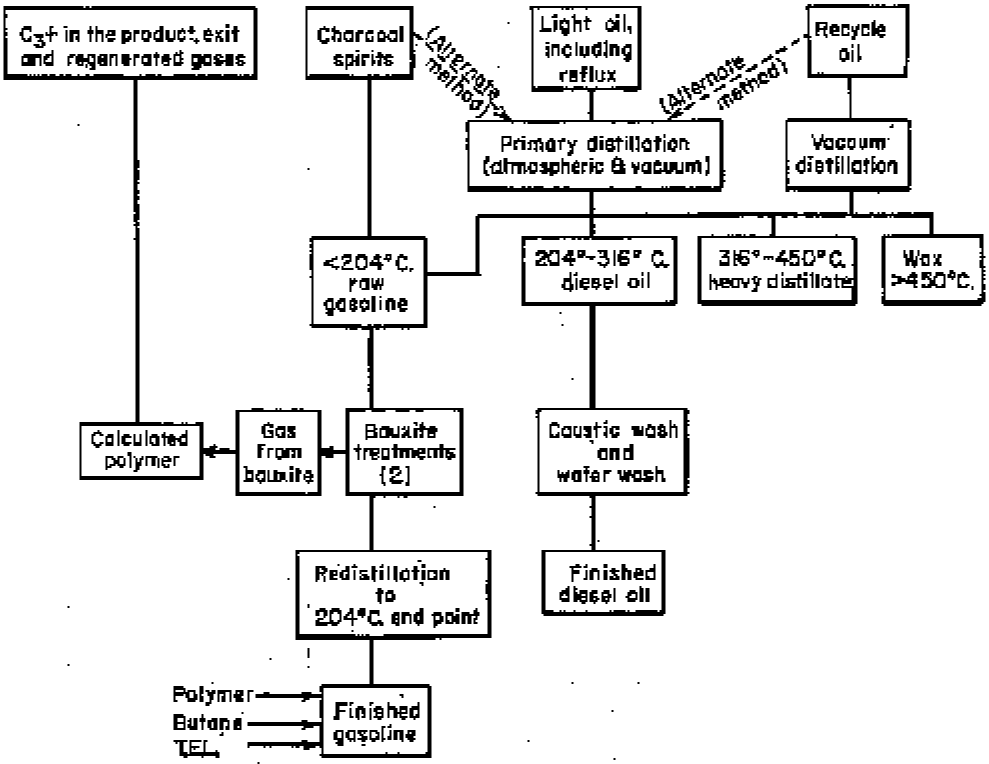

FIGURE 27.—Method for Separating Product Oils From Internally Cooled Converter.

The C_3 and C_4 olefins in the product gas recovered from the charcoal, as well as those remaining in the exit gas leaving the charcoal scrubbers, were accounted for in the final gasoline blend by adding a calculated amount of polymer gasoline after allowance for recovery losses.

The primary distillation for fractionation of the product streams was handled in either of two ways. Usually the light and reflux oils were blended and distilled separately from the recycle oil, which was of a much higher boiling range. An alternate method was to distill the gasoline from the mixture of light and reflux oils and then to add the recycle oil to the still pot and continue the distillation at reduced pressure until the diesel-oil end point of 316° C. was reached.

For fractionation of the gasoline and diesel oil, packed-glass columns having operating efficiencies of about 10 theoretical plates were used. The gasoline fraction (<204° C.) was separated at atmospheric pressure, while the diesel oil (204° to 316° C.) was recovered at 75 to 100 mm. of Hg. To separate the heavy distillate (316° to 450° C.) from the wax (>450° C.) a distillation was made in a vacuum still of about 1 theoretical plate at a pressure of 1 to 5 mm. of Hg. For this distillation the feed was either the recycle oil or the bottoms (>316° C.) from the primary distillation in the case where the recycle oil was added to the "topped" mixture of light oils.

TREATMENT AND EVALUATION

GASOLINE

Following primary distillation, the raw gasoline cut (<204° C.) was given a vapor-phase treatment over Cyclocel, an activated alumina, at 325° to 375° C., 25 p. s. i. g. pressure, and an hourly liquid space velocity of about 1.5. Yields of 90 to 95 percent of liquid products were obtained from this re-forming treatment. Because some high-boiling materials might be formed by polymerization of olefins, an ASTM distillation was made after re-forming to determine the quantity of polymers formed. If the ASTM distillation showed that the desired end point of 204° C. was exceeded, the material was redistilled in the 10-plate column to remove the polymer, which was collected as a residue. Raw and re-formed gasolines obtained with various feed gases are compared in table 37.

The bauxite treatment destroyed oxygenates in the raw gasoline and effected a desirable

TABLE 37.—*Effect of H_2:CO ratio and hourly space velocity of feed gas on properties of gasoline*

Experiment No.	31–C,[1] 1:1 gas		21–A,[2] 1.3:1 gas		26–A,[3] 0.7:1 gas		26–B,[4] 0.7:1 gas	
	Raw gasoline	Reformed gasoline	Raw gasoline	Reformed gasoline	Raw gasoline	Reformed gasoline	Raw gasoline	Reformed gasoline
ASTM distillation, °C.:								
First drop	37	37	52	33	--------	41	--------	29
5 vol.-percent	47	50	58	50	--------	51	--------	36
10 vol.-percent	54	59	62	58	--------	56	--------	41
20 vol.-percent	72	70	70	69	--------	66	--------	49
30 vol.-percent	89	82	79	79	--------	75	--------	58
40 vol.-percent	104	95	88	88	--------	86	--------	68
50 vol.-percent	120	107	100	99	--------	97	--------	79
60 vol.-percent	137	122	114	113	--------	111	--------	92
70 vol.-percent	153	139	130	133	--------	129	--------	114
80 vol.-percent	173	158	149	153	--------	154	--------	143
90 vol.-percent	194	181	173	176	--------	182	--------	179
End point	218	206	203	203	--------	211	--------	207
Recovered	97.5	97.5	98.0	97.0	--------	97.5	--------	96.5
Residue	2.0	2.0	2.0	3.0	--------	2.5	--------	2.5
Loss	0.5	0.5	--------	--------	--------	--------	--------	--------
Gravity °API	62.6	67.6	64.8	67.1	66.3	69.6	68.4	73.2
Bromine No.	91.7	126.0	70.8	123.5	111.4	88.7	113.1	131.5
Acid No.	8.6	0.07	1.6	0.20	0.31	0.0	0.30	0.0
Infrared analysis, wt.-percent of functional group:								
OH	2.6	0.28	4.2	0	0.18	0.2	0.25	0.04
CO	0.93	} 0	0.81	0.08	0.19	0	0.31	0.05
COOH	.4		0.2	0	0	0	0.11	0
COO	.56	0						
αC=C	12.7	1.2	9.2	1.2	1.1	0.63	1.8	0.25
βC=C	0.98	6.1	1.7	8.0	9.4	5.4	9.6	--------
Branched C=C	.38	1.6	0.59	1.4	0.9	2.6	0.69	0.73
Octane No. (motor)	--------	69.0	50.6	67.2	67.8	71.3	68.1	70.6
Reid vapor pressure p. s. i.	--------	8.0	8.1	9.3	--------	8.2	--------	11.7

[1] 600 S. V. H., recycle-gas ratio of 1.25 with removal of carbon dioxide, 400 p. s. i. g., 70-percent conversion, no bauxite unit.
[2] 100 S. V. H., recycle-gas ratio of 1 without removal of carbon dioxide, 300 p. s. i. g., 70-percent conversion, no bauxite unit.
[3] 600 S. V. H., recycle-gas ratio of 1 with removal of carbon dioxide, 400 p. s. i. g., 50 percent conversion, Cyclocel bauxite unit in service.
[4] 600 S. V. H., recycle-gas ratio of 1 with removal of carbon dioxide, 400 p. s. i. g., 90-percent conversion, Cyclocel bauxite unit in service.

isomerization by shifting the double bond from the terminal to an internal position, thereby boosting the octane rating. In experiments where the overhead vapors from the synthesis reactor had been Cyclocel-treated in place, as in experiments 26–A and 26–B, the raw gasoline already had a high content of β-olefins (β indicates the internal position of the double bond); only a slight amount of double-bond shifting occurred with the additional bauxite treatment. As shown in table 37, the ratio of β-plus branched-chain olefins to α-olefins was about 7.5 for the raw gasolines from experiment 26 but only 0.28 for that from experiment 21–A, where the vapors had not been treated in place. The total olefin content of the raw gasolines was the same in all cases with the total C=C grouping about 11.5 percent by weight (percent olefins$=\frac{\text{molecular weight}}{24}\times$ percent C=C). The properties of the reformed gasolines obtained after the bauxite treatments were similar for all three feed gases, the ratios of the β-plus branched-chain olefins to α-olefins were high, and the motor octane numbers were about 67 to 71. The improvement of the octane rating resulting from the Cyclocel treatment is shown for experiment 21–A, where an increase of over 16 numbers from 50.6 to 67.2 occurred. Where the treat-

TABLE 38.—*Properties of gasoline from 1.3H_2+1CO in experiment 21–A*

Description	Reid vapor pressure p. s. i.	Motor octane No. C.F.R.M.	Research octane No. C.F.R.R.
(1) Raw gasoline (original blend)	8.1	50.6	----------
(2) Reformed gasoline clear	9.3	67.2	----------
Plus 1 cc. T.E.L.	----------	75.8	----------
Plus 3 cc. T.E.L.	----------	81.6	----------
(3) Blend of 68 wt.-percent reformed gasoline plus 32 wt.-percent polymer gasoline clear	7.0	74.0	----------
(4) No. (3) plus butane clear	8.9	77.1	84.9
Plus 1 cc. T.E.L.	----------	83.6	91.2
Plus 3 cc. T.E.L.	----------	86.8	93.8

ment in place had been employed, a rise in octane of only about three numbers was effected by the additional Cyclocel treatment.

To account for the C_3 and C_4 olefins not recovered with the liquid products, an equivalent amount of commercial "cat poly" gasoline (30 to 35 percent by weight of the total gasoline), obtained from the Gulf Refining Co., was blended with the crude gasoline. The amount of polymer gasoline added was determined by assuming 85-percent conversion to poly gasoline of propylene and 95 of butylene, with recoveries of the 2 components from the gas stream taken as 80 and 90 percent, respectively. Since the octane rating of the blended gasoline would not be appreciably affected by the minor amounts of C_2 and C_4 gases, these were omitted to simplify blending. Table 38 shows the octane ratings and Reid vapor pressures of raw, re-formed, and blended gasolines from experiment 21. Addition of about 3.5 percent by weight of butane, available from the exit gases, to the mixture of re-formed and polymer gasoline increased the Reid vapor pressure to 9.9 pounds. ASTM distillation of the final blend (with added butane) is as follows: (API gravity 67.9 at 60° F.)

	° C.		° C.
First drop	41	50 vol.-percent	109
5 vol.-percent	49	60 vol.-percent	119
10 vol.-percent	59	70 vol.-percent	134
20 vol.-percent	74	80 vol.-percent	158
30 vol.-percent	88	90 vol.-percent	181
40 vol.-percent	99	End point	220
Recovered, percent			97

The octane values of the raw and re-formed gasolines are lower than those of Hydrocol gasolines (*11*), shown below. However, the antiknock ratings of the leaded, bauxite-treated gasolines are somewhat higher for the oil-circulation gasoline, indicating a greater lead susceptibility than for the Hydrocol product.

Octane rating of raw and treated Hydrocol gasoline

	Motor octane number, C. F. R. M.		
	Raw	Treated	Final blend [1]
Clear	62.0	75.9	80.2
Plus 1 cc. T. E. L.	70.1	80.5	
Plus 3 cc. T. E. L.	74.4	82.1	84.2

[1] Final blend contained 64 volume-percent of naphtha, 25 percent of C_3 to C_4 polymer, and 11 percent of n-butane.

A blended gasoline from experiment 31–C ($1H_2+1CO$), consisting of 65.6 percent by weight of re-formed gasoline and 34.4 percent polymer gasoline, was also tested. The values of the octane ratings, Reid vapor pressures, and gum stabilities are given in table 39. As these values corresponded very closely to those found previously (experiment 21–A), no additional blends were prepared. These gasolines would probably have the same lead susceptibility as those of experiment 21. The antiknock rating of the re-formed gasoline was independent of the H_2:CO ratio in the feed gas.

DIESEL OIL

The diesel fraction (204° to 316° C.), as recovered, was light yellow. After neutralization with caustic and water, the oil had the properties shown in table 40; corresponding United States Navy specifications are also listed. Although operating conditions varied considerably with the experiments, the diesel-oil characteristics did not. Except for a high pour point, these fuels met or surpassed United States Navy specifications.

HEAVY DISTILLATE AND WAX

The heavy distillate (boiling range, 316° to 450° C.) was a yellow semisolid at room temperature, with the properties given in table 41. The residue boiling >450° C. was a solid wax whose color varied with its iron content; the only properties that were measured were:

Experiment No.	21–A	31–C
Specific gravity at 60° F.	0.921	0.912
Kinematic viscosity at 120° C. (248° F.) centistokes	12.4	16.8
Melting point ° C.		115
Iron content percent		0.32

TABLE 39.—*Properties of gasoline from $1H_2+1CO$ in experiment 31–C*

	Reid vapor pressure, p. s. i.	Motor octane No., C. F. R. M.	Gum induction period,[1] minutes
Re-formed gasoline	6.0	66.0	
Blended gasoline [2]	7.66	71.4	207
Do.[3]	7.65	71.4	413

[1] ASTM D525-40; 60 minutes equivalent to 1 month storage.

[2] With gum inhibitor, ditertiary butyl para cresol, added in ratio of 0.2 lb. per 1,000 gal.

[3] With gum inhibitor, ditertiary butyl para cresol, added in ratio of 0.5 lb. per 1,000 gal.

In commercial operations heavy distillate and wax and perhaps diesel oil probably would be cracked. All of these fractions are quite amenable to thermal or catalytic cracking, generally producing higher yields of gasoline than are obtainable from petroleum cuts of corresponding boiling range.

TABLE 40.—*Properties of diesel oils from expanded-bed operation and U. S. Navy specifications for Premium-Grade diesel oil*

	Exp. 21-A[1]	Exp. 30-A[2]	Exp. 26-B[3]	Exp. 31-C[4]	U. S. Navy specifications
ASTM distillation, °C.:					
First drop	193	200		225	
5 vol.-percent	215	219		247	
10 vol.-percent	223	238		253	
20 vol.-percent	236	258		258	
30 vol.-percent	245	260		264	
40 vol.-percent	258	268		270	
50 vol.-percent	270	274		277	
60 vol.-percent	274	278		284	
70 vol.-percent	280	282		292	
80 vol.-percent	290	295		300	
90 vol.-percent	308	311		308	675° F. (357° C.) max. at 90 percent.
End point	315	349		318	
Recovered	97.5	97.5		98.0	
Gravity °API	47.5			44.6	
Viscosity:					
Kinematic at 38° C. (100° F.) centistokes	2.09			2.67	
Kinematic at 99° C. (210° F.) do	1.11			1.11	
Saybolt Universal at 38° C. (100° F.) sec.	34.3			35.0	35-45
Bromine No.	25.9			40.2	
Acid No.	1.1			0.15	
Cetane rating	79.0 (82.0 blending)	68.8	71.4	70.2	50
Pour point °F.	+20	+10	+18	+15	0° F., max.
Cloud point do		25	32		10° F., min.
Flash point—open cup	98° C. (208.4° F.)			112° C. (233.6° F.)	
Fire point—open cup	104° C. (219.2° F.)			128° C. (262.4° F.)	
Conradson carbon, 10 percent bottoms wt.-percent	Trace			0.0015	0.3

[1] 600 S. V. H., 1.3H₂:1CO, recycle-gas ratio of 1, 300 p. s. i. g., 70-percent conversion, without removal of carbon dioxide.
[2] 300 S. V. H., 0.7H₂:1CO, recycle-gas ratio of 1, 400 p. s. i. g., 90-percent conversion, Cycloral reactor at 325° C., with removal of carbon dioxide.
[3] 400 S. V. H., 0.7H₂:1CO, recycle-gas ratio of 1–1.25, 400 p. s. i. g., 90-percent conversion, Cycloral reactor at 325° C. with removal of carbon dioxide.
[4] 600 S. V. H., 1H₂:1CO, recycle-gas ratio of 1.25, 400 p. s. i. g., 70-percent conversion, with removal of carbon dioxide.

TABLE 41.—*Properties of heavy distillates from expanded-bed operation*

Experiment No.	21-A	31-C
ASTM distillation, ° C.:		
First drop	310	332
5 vol.-percent	345	346
10 vol.-percent	355	357
20 vol.-percent	362	365
30 vol.-percent	370	374
40 vol.-percent	378	380
50 vol.-percent	389	388
60 vol.-percent	398	395
70 vol.-percent	406	408
80 vol.-percent	420	416
90 vol.-percent	432	429
End point	450	450
Recovered	98.0	99.0
Gravity ° API	37.8	39.1
Kinematic viscosity, at 120° C. (248° F.)—centistokes (extrapolated)	1.27	2.11
Conradson carbon wt.-percent	0.01	Trace
Pour point ° C.	33	Semisolid at room temp.

OXYGENATED COMPOUNDS

Along with hydrocarbons, several types (particularly alcohols and acids) of essentially aliphatic oxygenated compounds are synthesized over iron and distributed between the oil and aqueous streams (*12, 18, 33, 42*). Recovery of aqueous oxygenates is commercially feasible, but the recovery of oil-soluble oxygenates, principally higher boiling acids, esters, and alcohols, is more difficult. To gain information about the yields of these materials, infrared analyses were made and acid numbers determined for the raw oils; carbon percentages and acid numbers of aqueous product were obtained in fixed-bed experiments; and mass-spectrometer analyses identifying individual components in this material were available for the expanded-bed experiments.

Infrared analysis of the light oil was used to determine weight-percentages of functional groups (CO, OH, COOH, COO). Since most of the oxygenates could be removed from this oil by water washing, it was deduced that they were predominantly the lower molecular weight homologues. Therefore, acetone, ethyl alcohol, acetic acid, and ethyl acetate were selected to estimate the yield of oxygenates in the light oil. Oxygenates in recycle oil were estimated from the acid number, assuming acetic acid to be present; infrared analyses ordinarily were not made for this stream. Only minor amounts of oxygenates were present in recycle oil because of its high boiling range with generally 80 to 90 percent or more boiling >250° C., as shown by infrared analysis of oil from experiment 19:

	Weight-percent
$\alpha C=C$	0.34
$\beta C=C$	3.0
COOH and CO	.37
COO (esters)	.34
OH	.09

TABLE 42.—*Analyses of liquid products from expanded-bed experiments*[1]

Experiment No.	26-A[2]	30-B[3]	31-C[4]	19[5]
Pilot plant	2	3	3	2
Recycle oil:				
Bromine No.	28.6	16.9	9.9	22.3
Acid No.	0.60	0.44	0.37	0.41
Light oil:				
Bromine No.	------	52.3	63.7	75.2
Acid No.	------	3.1	13.9	1.7
Infrared analysis, wt.-percent of functional groups:				
OH	3.7	1.3	2.5	2.2
CO COOH	1.5	0.71	0.49	0.61
COO	0.97	0.54	0.38	1.14
αC=C	4.9	7.3	7.4	4.5
βC=C	2.4	1.9	1.3	6.0
Branched C=C	0.90	0.86	0.73	------
Calculated bromine No.	49	62	63	67
Reflux oil:				
Bromine No.	24.4	(6)	(6)	27.8
Acid No.	3.5	------	------	3.0
Infrared analysis, wt.-percent of functional groups:				
OH	1.0	------	------	1.0
CO COOH	0.35	------	------	0.47
COO	0.30	------	------	0.15
αC=C	2.2	------	------	1.0
βC=C	4.8	------	------	2.6
Calculated bromine No.	37	------	------	31
Aqueous layer, wt.-percent:[7]				
H_2O	88.8	92.2	90.1	94.6
Acetic acid	2.6	1.6	1.5	0.9
Propionic acid	0.3	------	------	------
Acetone	0.1	0.2	0.2	0.1
Methyl ethyl ketone	------	0.1	------	------
C_1OH	1.2	0.7	0.4	0.7
C_2OH	4.8	3.4	5.4	2.5
n-C_3OH	1.6	1.1	1.2	0.8
n-C_4OH	0.7	0.5	0.6	0.5
n-C_5OH	0.3	0.2	0.3	------
n-C_6OH	------	0.4	------	------

[1] 400 S. V. H., 70-percent conversion, fused iron, without bauxite unit.

[2] $0.7H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 400 p. s. i. g., 238° C. maximum temperature, 0.72 usage ratio.

[3] $0.7H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 450 p. s. i. g., 251° C. maximum temperature, 0.83 usage ratio.

[4] $1H_2$:1CO, recycle-gas ratio of 1.25 with removal of carbon dioxide, 400 p. s. i. g., 251°–258° C. maximum temperature, 0.93 usage ratio.

[5] $1.3H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 300 p. s. i. g., 244°–245° C. maximum temperature, 1.04 usage ratio.

[6] Not a product stream for operation of the barrel-per-day plant.

[7] Determined by mass spectrometer.

Amounts of water-soluble compounds during fixed-bed operation were estimated from carbon determinations and acid numbers; only ethyl alcohol and acetic acid were assumed to be present. This information, of course, had limited value but indicated trends and relative production of oxygenated material. From the mass spectrometer analyses of the aqueous products obtained during expanded-bed experiments, yields of individual oxygenated components, such as acetic and propionic acids, ethyl and propyl alcohols, and acetone, were calculated.

Typical infrared analyses of light oils and mass-spectrometric analyses of aqueous products are given in table 42; calculated specific yields of oxygenates are presented in table 43. The major portion of oxygenates was usually concentrated in the aqueous layer (in experiments 26–A and 30–B, 75 to 80 percent by weight; in experiment 19 about 60 percent). However, in experiment 31–C oxygenates were divided about equally between the oil and aqueous streams. Of the oxygenated compounds, alcohols predominated, averaging 75 percent by weight. Specific yield of oxygenates (8.1 gm. per m.³) from the small plant in experiment 26–A compared favorably with that of 7.2 gm. per m.³ from the barrel-per-day plant in experiment 30–B, in both of which $0.7H_2+1CO$ was employed. Although more oxygenates were produced with $1H_2+1CO$, the specific yield of 17.4 gm per m.³ (about 10 percent of the C_3+ product) in experiment 31–C was unexpectedly high.

Considering the total C_3+ production, including both the hydrocarbons and oxygenated compounds (excluding water), the breakdown between hydrocarbons and oxygenates shown in table 44 is obtained. The values shown in table 44 assume that all of the oxygenated compounds were in the gasoline boiling range.

TABLE 43.—*Calculated specific yields of oxygenated compounds for expanded-bed experiments*[1]

(grams per cubic meter)

Experiment No.	26-A[2]	30-B[3]	31-C[4]	19-A, B, C[5]
Aqueous layer:				
H_2O	45.80	86.70	80.20	109.70
Acetic acid	1.34	1.50	1.35	1.05
Propionic acid	.17	------	------	------
Acetone	.06	.14	.18	.12
Methyl ethyl ketone	—	.07	------	------
C_1OH	.63	.61	.72	.81
C_2OH	2.47	3.19	4.81	2.89
n-C_3OH	.83	.80	1.06	.92
n-C_4OH	.36	.22	.45	.58
n-C_5OH	.17	.14	.27	------
n-C_6OH	------	.30	------	
Total water-soluble oxygenates	5.79	4.72	8.90	6.34
Heavy oils: Acetic acid[6]	.07	.05	.01	.02
Light oil:				
Acetic acid	.35	.27	.00	.36
Ethyl alcohol	1.27	.88	5.02	2.45
Acetone	------	------	1.28	------
Ethyl acetate	.22	.32	.03	1.17
Total oil-soluble oxygenates	1.85	1.47	6.33	4.01
Total yield of oxygenates (excluding H_2O)	8.1	7.2	17.4	10.4

[1] 400 S. V. H., 70-percent conversion, fused iron, without bauxite unit.

[2] $0.7H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 400 p. s. i. g., 238° C. maximum temperature, 0.72 usage ratio.

[3] $0.7H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 450 p. s. i. g., 251° C. maximum temperature, 0.83 usage ratio.

[4] $1H_2$:1CO, recycle-gas ratio of 1.25 with removal of carbon dioxide, 400 p. s. i. g., 251°–258° C. maximum temperature, 0.93 usage ratio.

[5] $1.3H_2$:1CO, recycle-gas ratio of 1 with removal of carbon dioxide, 300 p. s. i. g., 244°–245° C. maximum temperature, 1.04 usage ratio.

[6] Calculated from acid No. and assumed to be acetic acid.

[7] Includes yields calculated for "reflux-oil" stream.

TABLE 44.—*Distribution of oxygenates and C_4+ hydrocarbons for expanded-bed experiments*

Experiment No.	26-A	30-B	31-C	19 A, 19-B, 19-C
H_2:CO in feed gas	0.7	0.7	1.0	1.3
Hydrocarbons, wt.-percent:				
Gasoline (C_4+)	40.9	38.7	46.2	47.7
Diesel oil	15.1	16.5	22.6	11.0
Heavy distillate	24.0	14.8	10.7	12.9
Wax	15.4	21.2	5.9	19.3
Oxygenated compounds, wt.-percent:				
Oil-soluble	1.1	0.8	5.2	2.2
Water-soluble	3.6	3.0	5.4	3.6

INFLUENCE OF OPERATING VARIABLES ON DISTRIBUTION OF PRODUCTS

The principal operating variables affecting the distribution of products were pressure, H_2:CO ratio in the feed gas, and temperature. No definite trend in product distribution due to variation of the gas throughput, between the limits of 600 and 1,000 space velocity, was established. The effect of pressure upon the distribution of products, namely, a shift toward the production of heavier hydrocarbons with increased pressure, has been discussed previously and is illustrated by the data of table 25 (see p. 36). In table 18 (see p. 44) variation in the product distribution resulting from changes in the H_2:CO ratio of the feed gas during experiments 19, 22, and 26 is shown. As the proportion of carbon monoxide was increased, the production of heavier hydrocarbons increased. This effect was most pronounced when the feed gas was rich in carbon monoxide, as shown by the relatively low proportion of gasoline produced with $0.7H_2+1CO$ gas.

A detailed study of the effect of temperature on the product distribution was made in experiments 26-A and 26-B in which $0.7H_2+1CO$ gas and carbon dioxide scrubbing were used (table 45 and figs. 28 to 30). At the higher temperatures (and conversions) somewhat more C_1 plus C_2 hydrocarbons and appreciably more gasoline were produced, while the middle fractions (diesel oil and heavy distillate) remained about the same. Similar effects may be expected with $1H_2+1CO$ or $1.3H_2+1CO$. The specific yield of C_1 plus C_2 hydrocarbons increased from 21-25 (at an hourly space velocity of 600 and temperature 238° to 258° C.) to 23-29 gm. per m.^{3} (at 900 hourly space velocity and 259° to 275° C.), and by an additional 4 to 5 gm. per m.^{3} when bauxite was used in place. The amount of gasoline varied from 43 to 64 weight-percent, independently of space velocity, when the temperature varied from 238° to 281° C. The raw gasolines produced at these conditions were highly olefinic, possessing an ASTM bromine number of about 112. After vapor-phase re-forming over Cycloel at 375° C. and without addition of polymer, they had a motor octane rating of about 71 (Reid vapor pressure, about 10.0 pounds). The diesel oil was similar to that produced from $1H_2+1CO$, with an octane rating of 70 to 75 and a pour point of 10° to 15° F. As figure 30 shows, virtually all of the products were hydrocarbons. No appreciable variation was observed in the production of oxygenates (oil- and water-soluble) whose specific yield was only about 7 to 8 gm. per m.^{3} (calculated without the bauxite unit in service). The theoretical limit of hydrocarbon production is 208 gm. per m.^{3} (S. T. P.) of $0.7H_2+1CO$.

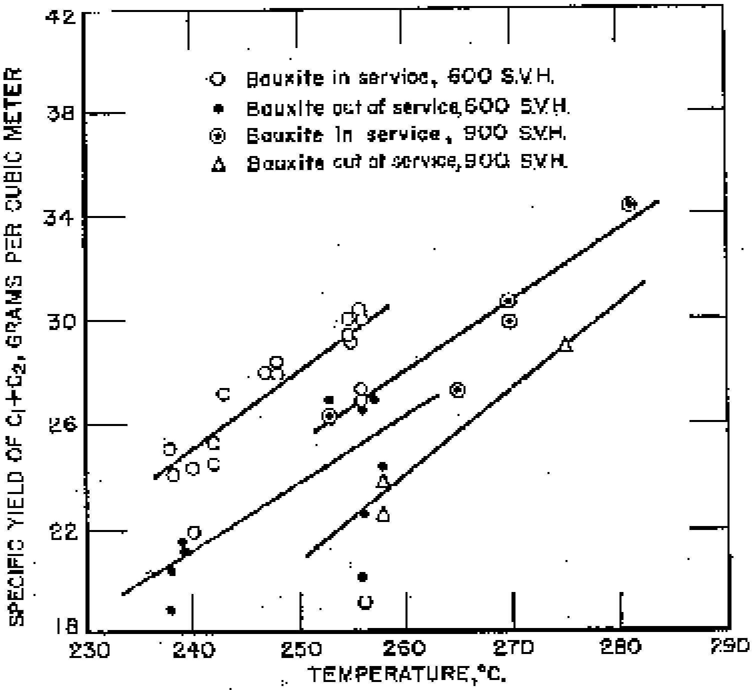

FIGURE 28. Effect of Temperature on Gas Yields With $0.7H_2+1CO$ Synthesis Gas.

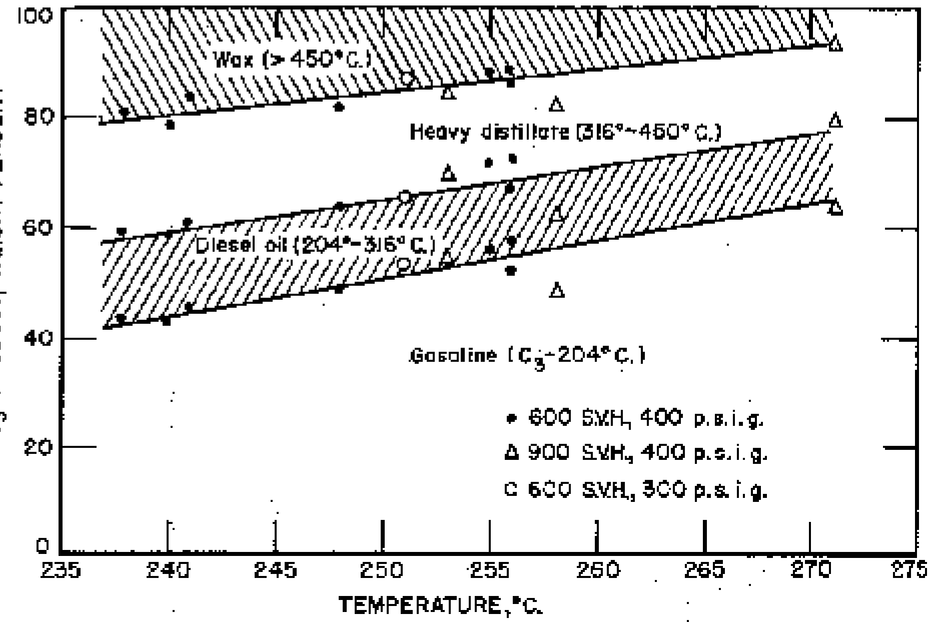

FIGURE 29.—Effect of Temperature on Distribution of C_3^+ Products With $0.7H_2+1CO$ Synthesis Gas.

TABLE 45.—*Average conditions and yields during steady operating periods in experiments 26–A and 26–B*

[Synthesis gas, ratio in fresh gas, H_2:CO, 0.7]

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Duration .... hr..	169	47	46	69	54	97	204	40	47	368	70	73	69	8
Operating reactor, temperature .... °C..	326	326	326	326	325	325	325	Out	Out	326	300	300	300	300
Catalyst, age for period .... hr..	92	265	306	364	456	560	609	639	674	1,038	1,285	1,351	1,376	1,462
Synthesis gas:														
S. V. H. (settled bed)...	590	590	596	599	606	600	600	803	595	590	602	897	894	897
Conversion vol.-percent H_2+CO...	67.5	68.9	77.2	80.7	90.0	65.5	79.7	65.0	83.7	68.1	69.8	85.5	87.7	88.2
Usage ratio H_2:CO......	0.72	0.71	0.72	0.69	0.66	0.71	0.68	0.73	0.49	0.74	0.71	0.60	0.68	0.69
Gas-recycle [2] ratio........	1	1	1	1	1	1	1.5	1	1.5	–	1	1	1–1.0	1.5
Pressure, maximum p.s.i.g...	395	408	406	402	404	406	400	398	400	409	411	414	416	417
Temperature, °C.:														
Maximum...........	261	242	245	256	266	255	256	259	275	241	253	266	271	281
Differential..........	5	5	5	5	5	4	6	6	5	4	5	6	7	7
Yields, specific, gm./m.³:														
CH_4........	14.8	12.2	13.4	14.7	13.9	13.1	12.8	11.4	18.0	12.4	14.5	16.3	17.6	20.7
$C_2H_4+C_2H_6$...........	16.0	12.6	14.7	15.4	12.5	11.7	11.6	11.8	17.2	12.6	11.3	11.0	11.8	12.5
C_3H_6...........	6.7	3.2	6.2	4.8	8.7	8.6	6.8	8.5	3.9	4.6	4.9	9.0	11.5	......
C_3H_8...........	11.7	8.8	11.4	13.2	8.6	6.0	10.8	14.0	17.0	11.9	11.2	11.8	10.3	....
C_4H_8...........	4.1	1.9	3.3	3.8	2.1	6.2	2.6	5.0	1.8	5.7	4.2	3.8	4.5	....
C_4H_{10}...........	11.6	9.1	11.4	11.7	5.5	10.2	7.5	8.6	16.7	5.9	11.5	8.0	6.4	....
Products. Distribution of C_3+ wt.-percent:[3]														
Gasoline (C_3–)........	53.9	43.2	48.8	56.7	57.3	45.6	51.3	45.5	62.8	50.4	54.9	....	59.3	....
Diesel oil............	12.3	15.6	14.4	15.6	15.1	15.7	14.9	13.4	11.7	15.6	14.8	....	14.0	....
Heavy distillate......	21.5	19.9	18.4	16.0	14.7	21.6	18.8	23.3	11.4	18.1	15.8	....	19.7	....
Wax............	13.6	21.3	18.4	11.8	13.0	17.1	14.3	17.7	13.1	16.0	15.5	....	7.0	....

[1] Reactor in intermittent service. [2] With removal of carbon dioxide. [3] Includes oil-soluble oxygenates.

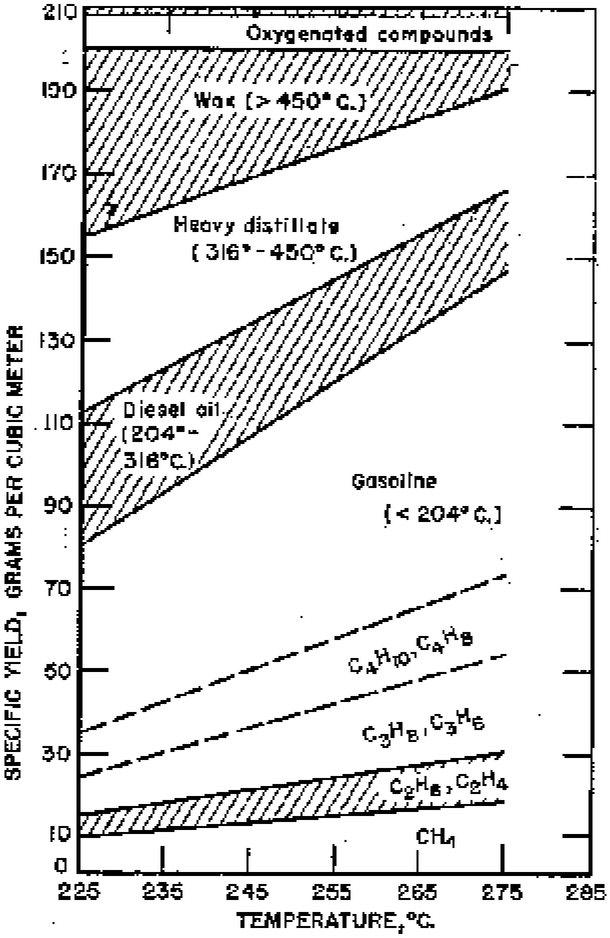

FIGURE 30.—Effect of Temperature on Specific Yields With $0.7H_2+1CO$ Synthesis Gas.