TABLE 5.—*Conversion of synthesis gas as a function of hourly space velocity with cobalt in experiment 6*

Experiment No.	6-B	6-C	6-D	6-E
Synthesis gas:				
S. V. H. (settled bed)	102	260	438	600
Conversion, vol.-percent H_2+CO	87	46	37	33
Pressure, average, p. s. i. g.	83	318	190	170
Temperature, °C.:				
Average	183	192	201	204
Maximum	202	210	220	230
Yields:				
Specific, gm. C_1+C_2 per m.³	29.8	41.9	57.9	32.6
Space-time of C_3+, kg. per m.³ settled cat. vol. per day calculated	240	428	595	597

Although cobalt was found durable in experiments 1 to 5, further experimentation with this material was not carried out, except for a short test (experiment 6). As in the dry-bed experiments with cobalt, the liquid products were essentially completely saturated, as shown by the data of table 6. This meant production of a poor quality of gasoline with a low octane rating. The more important and motivating reasons for discontinuing the use of cobalt were concerned with its high cost, the prohibitive amounts that would be required for large-scale operation, and the potential scarcity in a time of national emergency.

TABLE 6.—*Distribution of products from concurrent operations with cobalt*

(Weight-percent of total hydrocarbons)

Experiment No. Component	2-F (S. V. H., 102)	3-C (S. V. H., 281)
CH_4	18.5	15.9
C_2H_6	3.1	5.8
C_2H_4	.0	.0
C_3H_8	6.4	5.3
C_3H_6	1.0	.1
C_4H_{10}	7.4	7.2
C_4H_8	.7	1.8
C_5H_{12}	4.3	7.2
C_6H_{14}	4.3	5.2
C_7H_{16}	2.0	5.0
i-C_8H_{18}	3.5	4.3
n-C_9H_{20}	2.2	3.1
n-$C_{10}H_{22}$	3.3	4.0
n-$C_{11}H_{24}$	3.8	3.5
n-$C_{12}H_{26}$	2.7	3.5
n-$C_{13}H_{28}$	3.3	3.1
n-$C_{14}H_{30}$	3.3	3.1
n-$C_{15}H_{32}$	2.2	2.2
n-$C_{16}H_{34}$	3.3	2.6
n-$C_{17}H_{36}$	2.2	2.6
n-$C_{18}H_{38}$	2.1	2.2
n-$C_{19}H_{40}$	2.1	.9
n-$C_{20}H_{42}$	.5	.4
Wax	17.8	11.5
Total	100	100

As shown by the data of table 4, precipitated-iron catalysts required operating temperatures 50° to 60° C. higher than cobalt to secure comparable productivity. Higher boiling cuts of oil had to be used as coolant. Despite the increased temperatures, the specific yields of C_1 plus C_2 (25 to 35 gm. per m.³) were almost always less than those obtained with cobalt (table 3). Whereas the usage and feed-gas ratios always were similar in the cobalt tests, the usage ratio now lagged considerably. Major difficulties that had not been encountered with cobalt were disintegration and agglomeration of pelleted as well as granular precipitated iron; eventually a prohibitive pressure drop across the bed resulted.

These experiments led directly to the abandonment both of precipitated-iron catalysts and trickle-flow cooling for the remainder of the pilot-plant development. In all subsequent experiments to be discussed the submerged-bed principle was employed to effect temperature control; and the catalysts were prepared by fusion of iron oxide, except in the preliminary tests, where both pelleted cobalt and precipitated granular iron were used.

SUBMERGED, FIXED-BED EXPERIMENTS

PRELIMINARY TESTS

To determine whether temperature control could be improved by completely submerging the catalyst in the cooling medium, several submerged-bed tests were made with the same apparatus, and the same type of catalysts and cooling oil as described for the trickle-flow experiments.

The initial tests (experiments 5-F and 6) were made with pelleted cobalt. The catalyst for experiment 5-F had been used previously in trickle-flow operation, while that for experiment 6 was a fresh catalyst reduced with hydrogen. The gas saturator was bypassed during these tests, and the gas was fed directly at the bottom of the converter. The operating procedure was the same as that described for trickle-flow operation. The temperature was still controlled by varying pressure since evaporative cooling was employed. Vapors and unreacted gas left the reactor overhead and flowed to the condenser from which the condensate was returned to the reactor by a circulating pump. In experiment 5-F the liquid was returned to the top of the reactor, while in experiment 6 it was sent in at the bottom. At gas rates lower than an hourly space velocity of 300, excellent temperature control was attained; significantly, the activity of the catalyst was unimpaired. However, when this gas rate was exceeded, the gas tended to dry the catalyst at the entrance of the converter, as it had in trickle-flow operation, and a localized hot spot was produced at that point. Quenching of the hot spot was accomplished by reducing the gas flow, thus allowing the liquid to flood the catalyst.

The next submerged-bed test (experiment 9–C) was made with the used, precipitated-iron, granular catalyst from trickle-flow experiment 9–B. In this experiment the pressure drop along the converter had increased more than desired, but the catalyst was still active. To avoid hot spots near the gas entry, and, equally important, to insure adequate distribution of cooling liquid throughout the entire bed, the cooling oil was taken from the top of the converter and circulated upward through the catalyst by means of a pump. The gas was sent through the saturator before it entered the bottom of the converter as a further precaution against the possibility of drying the catalyst. Severe physical disintegration of the catalyst and buildup of a prohibitive pressure differential through the bed necessitated a shutdown after only about 1 week of operation in this manner, but enough information was obtained at hourly space velocities of 100 and 200 to show that the catalyst activity was unimpaired by submersion in oil. Further experimentation with this type of system appeared very desirable with catalysts more resistant to disintegration.

APPARATUS

Equipment used for the submerged, fixed-bed experiments was essentially the same as that used previously for trickle flow, but a pump was added for circulating the cooling medium through the catalyst, as shown in figure 6. Also, the oil from the overhead, water-cooled condenser was now refluxed into the recycle-oil line on the suction side of the circulating pump, rather than, as previously, through a separate pump and preheater into the top of the converter. Gas and cooling oil flowed cocurrently from the bottom to the top of the converter.

For experiments 10 to 12, a 4-inch layer of Aloxite (2- to 7-mesh) was used beneath the catalyst for dispersing the gas. Because Aloxite disintegrated, ⅛-inch and/or ¼-inch steel shot, each layer 3 to 6 inches deep, was substituted, beginning with experiment 13. In experiments 10 and 11 the gas was passed first through a "saturator," where it was saturated at high temperatures with hydrocarbon vapors to avoid evaporative cooling and the attendant danger of dry spots occurring at the bottom of the catalyst bed. After the applicability of the principle of nonevaporative cooling had been demonstrated in experiment 11, this saturator was no longer needed and was removed before

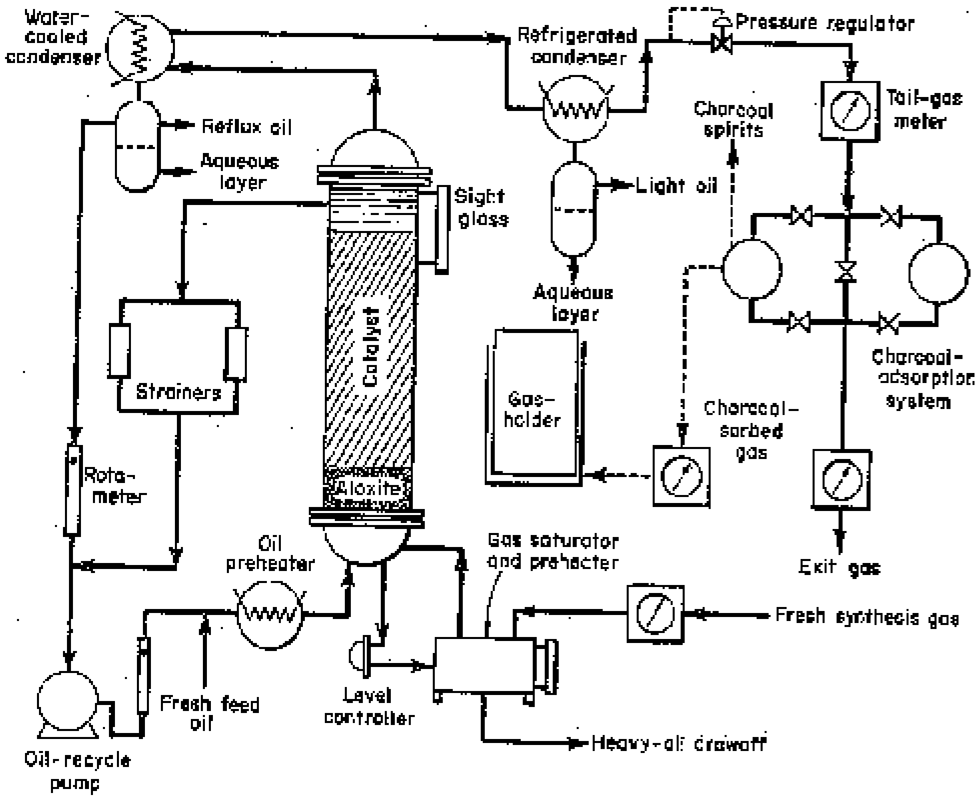

FIGURE 6.—Submerged, Fixed-Bed Process.

experiment 12.[5] Thereafter, gas was preheated to reaction temperature by means of an electric heater. Another minor modification made at the time of experiment 12 was to return the reflux oil directly to the top section of the converter rather than to the recycle-oil line. Because of the heat losses inherent in small pilot plants, the recycle oil had to be preheated to converter temperature. During experiments 10 to 12, an electric immersion heater was employed; at the start of experiment 13, this preheater was replaced by a coil heated with Dowtherm. This change was made to prevent cracking of the recycle oil at the higher temperatures on the surface of the immersion heater. In large-scale operation, cooling of this oil stream would be required, since as much as 90 percent of the heat of reaction could be removed by circulating oil and recovered by generating high-pressure steam. Starting with experiment 14, provision was made for recycling the tail gas to the bottom of the converter by means of a recycle compressor. At about the same time a second internally cooled pilot plant, similar to the original already described, was completed and used for experiment 15.

Products and unreacted gas passed overhead to the condensing system in which gases and liquid products were separated in the water-cooled condenser operated at 40° to 45° C., and in the refrigerated condenser operated at 5° C. The liquid products consisting of oil, water, and oxygenated organic compounds flowed by gravity into traps beneath the condensers, where, because of immiscibility, rapid separation into aqueous and oil layers occurred. The aqueous layer, which contained most of the oxygenates, was withdrawn regularly from each trap, as was the entire amount of oil collected in the refrigerated condenser trap (light oil).

All of the oil from the water-cooled condenser trap (reflux oil) was returned as a measured stream either into the recycle-oil line or to the top of the converter, as was mentioned. When evaporative cooling was employed in experiment 10, this reflux stream aided primarily in maintaining the liquid level in the converter and considerably reduced the amount of fresh feed oil that otherwise would have been required. With nonevaporative cooling, as employed thereafter, this reflux was not usually required to maintain the liquid level in the converter, but rather served to retain a certain amount of relatively light material in the coolant and prevent the buildup of too great a concentration of high-boiling products.

Withdrawal of heavy oil depended on the mode of cooling selected. With evaporative cooling the heavy product oil was removed frequently from the saturator to maintain a relatively low boiling, volatile coolant in the reactor. When nonevaporative cooling was used, the heavy oil was drained only to maintain a constant level in the converter. A certain concentration of heavy material and wax was thus intentionally built up and retained in the coolant to facilitate this mode of operation.

The gas leaving the condensing system was passed through a back-pressure regulator to a recovery system where activated charcoal removed almost all of the uncondensed C_3+ gaseous hydrocarbons. This system consisted of 2 parallel vessels, each of 1 cu. ft. capacity, which were used alternatively. Each had an absorption cycle of 8 hours. The exit gas was metered, sampled for analysis, and rejected to the atmosphere. The material retained by the charcoal was stripped by means of superheated steam. The heavier fraction was condensed in a refrigerated trap; the lighter portion, mainly C_3 and C_4 components, was metered and collected in a gas holder.

RAW MATERIALS

SYNTHESIS GAS

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

CATALYST

Commercial, synthetic-ammonia-type iron catalysts were tested first because they seemed to have the hardness and physical strength required for submerged-bed operation. The chemical analyses of two such catalysts, Bureau of Mines Nos. D-3001 and D-3006, are given in table 7. The composition of these catalysts was virtually identical. Their bulk densities (4- to 6-mesh granules) were 176 (D-3001) and 145 lb. per cu. ft. (D-3006). This particle size was used in all fixed-bed experiments except 16, in which 2- to 4-mesh particles were employed. Although catalysts discharged after 2 or 3 months of operation showed little evidence of loss of strength or hardness, considerable reduction in the size of the particles occurred. For example, a charge of 4- to 6-mesh catalyst showed the sieve analysis given in table 8 after 2,300 hours of operation in experiment 14.

The catalysts were reduced with hydrogen

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[5] First submerged-bed experiment conducted at the Bruceton, Pa., station.

before exposure to synthesis gas. Reduction conditions were as follows:

Experiment No.	10 to 13	14 to 17
Temperature, °C	450–500	450–600
Pressure, atm	1	1
Duration, hr	34–50	61–70
Space velocity, hr⁻¹	1,300–1,500	1,700–2,000
Moisture content [1] of inlet hydrogen [2], gm. H_2O per m^3	1–2	<0.3–0.4
Reduction of iron, weight-percent	90–93	93–98

[1] Measured amount.
[2] Recycle plus makeup.

TABLE 7.—*Analyses of raw, synthetic-ammonia-type iron catalysts*
(Weight-percent)

	D-3001	D-3006
Total Fe [1]	67.35	68.62
MgO	4.56	4.60
SiO_2	.99	1.08
K_2O	.52	.49
Cr_2O_3	.54	.56

[1] Of the total Fe present as oxide, about ⅔ was ferric and ⅓ ferrous.

TABLE 8.—*Sieve analysis of used, synthetic-ammonia-type iron catalyst (originally 4- to 6-mesh)*

Mesh size	Weight-percent	Mesh size	Weight-percent
4–6	15.5	20–35	15.9
6–12	25.3	35–100	14.2
12–20	15.2	<100	13.9

A typical analysis of the hydrogen was:

	Volume-percent
Hydrogen	99.2
Nitrogen	.6
Oxygen	.2
Carbon monoxide	Trace
Carbon dioxide	Do.

In the initial experiments (10 to 13) this operation was conducted in the converter; beginning with experiment 14, a separate 4-inch-diameter unit with capacity for a charge of about 0.35 cu. ft. of catalyst was used for this purpose, as shown schematically in figure 7.

Recycling the exit gas during all of the reduction treatments substantially decreased the consumption of hydrogen. As an example, in experiment 14 the fresh hydrogen constituted only 6 volume-percent of the total gas flow. Essentially the only fresh hydrogen required with this type of system was an amount equivalent to that converted to water by the reduction of the oxide:

$$Fe_3O_4+4H_2 \rightarrow 3Fe+4H_2O.$$

Recycle was made possible by drying the gas after its passage through the hot catalyst. Drying was accomplished by cooling and compression. In all experiments of this series preliminary drying was effected by cooling the gases from the reductor at substantially atmospheric pressure by passing them through a water-cooled condenser operated at 30° to 35° C. and then through a refrigerated condenser operated at 5° C. The final drying operation followed compression. In experiments 10 to 13 the gas was compressed to 125 p. s. i. g. and then cooled to 35° C. before expansion and return to the reductor. In experiments 14 to 17 compression to 350 p. s. i. g. was followed by cooling to 5° C. Throughout this series

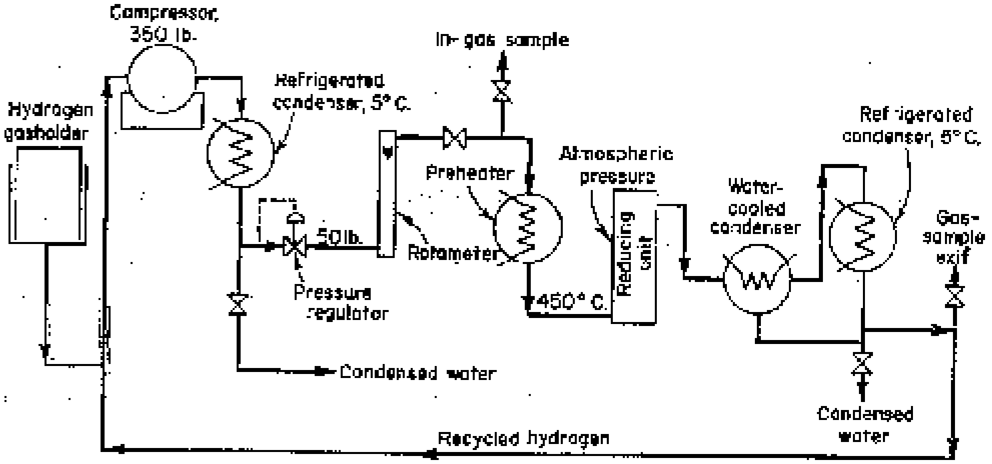

FIGURE 7.—Catalyst-Reduction Unit for Internally Cooled Converters 1 and 2.

makeup hydrogen was introduced into the main stream on the suction side of the compressor.

Reduction was usually continued until the moisture content of the exit gas did not exceed that of the inlet gas by more than 0.1 or 0.2 gm. of water per m.^{3} For experiments 10 to 13, 90- to 93-percent reduction of iron was achieved; in experiments 14 to 17, 93- to 98-percent. Three operating variables may have contributed to this improvement: Increased hydrogen throughput, reduced moisture content of the inlet gas, and extended time for treatment.

Following reduction the catalyst was cooled to room temperature in hydrogen. When the reduction had been conducted in place, the converter was flooded with carbon dioxide and maintained at a slight positive pressure under this protective atmosphere until synthesis was begun. When the reduction had been conducted in the external reductor, the cooled, reduced catalyst was discharged under carbon dioxide into gastight containers and stored until it was needed for use. The containers were maintained under several pounds pressure of carbon dioxide to protect the contents against atmospheric oxidation while in storage.

COOLING OIL

In the initial experiment of this series (experiment 10), in which heat of reaction was removed mainly by vaporization of cooling oil, a petroleum naphtha cut boiling at 195° to 205° C. was charged as the cooling medium. It was expected that coolant boiling in this range would limit the temperature increase resulting from the synthesis reaction to not more than 10° C.; heat dissipation was assumed to be effected only by evaporative cooling.

This same type and cut of petroleum naphtha was also used as the cooling oil in experiment 11, in which the heat of reaction was removed essentially as sensible heat for the first time. Higher boiling cooling oils were selected thereafter. In experiments 12 and 13 a commercial mineral oil, Primol D (200° to 400° C.), was used. For experiment 14 a fraction (250° to 300° C.) of synthetic diesel fuel, produced in a Fischer-Tropsch plant at Harnes, France, served as coolant. The Harnes plant employed cobalt catalyst. For all work after experiment 14 oils of the desired boiling range (300° to 450° C.) were prepared from the products of preceding experiments. After a few days of synthesis in all experiments except possibly experiment 10, most of the original oil appeared to have been replaced by products of reaction. In other words, a steady state was reached in which the material produced by the synthesis was the source of the coolant and the process was self-sustaining until terminated with all of the coolant required produced by synthesis. A typical steady-state recycle oil (heavy oil) from experiment 15 showed the following characteristics:

Gravity ° API	39.0
Simple vacuum distillation ° C. (corrected to 1 atm.):	
First drop	301
5 volume-percent	340
10 volume-percent	353
20 volume-percent	370
30 volume-percent	384
40 volume-percent	400
50 volume-percent	417
60 volume-percent	443
63 volume-percent	450
Kinematic viscosity at 120° C. (248° F.) centistokes	4.48

In fixed-bed experiments employing nonevaporative cooling a flow rate of 35 to 50 gal. per hr. of oil maintained a temperature differential of 15° to 20° C. between the top and bottom of an 8-foot catalyst bed at 70-percent conversion of the synthesis gas flowing at an hourly space velocity of 300 in terms of fresh gas. This flow of liquid corresponded to a velocity of 0.028 to 0.040 ft. per sec. based on the total cross-sectional area of the converter.

OPERATION

EVAPORATIVE COOLING

As in the trickle-flow experiments, heat dissipation and temperature control were again effected by evaporative cooling in the first submerged-bed run, experiment 10. Since the temperature depended on the pressure, simultaneous changes of both variables were required. The procedure employed will be discussed briefly.

After the catalyst had been reduced in the converter, cooling oil (boiling at 195° to 205° C.) was charged to the overflow level while an adequate flow of nitrogen was maintained. The temperature was raised to about 200° C. by passing the oil through the preheater and by preheating the gas in the saturator. At this temperature, pressure was increased to between 50 and 60 p. s. i. g., and $1H_2+1CO$ gas was introduced at an hourly space velocity of 100. The pressure was raised in increments to about 80 p. s. i. g., so that the temperature increased quickly to between 260° and 270° C. After these conditions had been maintained for several days and a steady state had been established, the space velocity was increased to 200. To maintain 265° C. at this flow rate the pressure had to be raised to 100 p. s. i. g. Upon completion of a brief period of operation at a space velocity of 200, the rate was increased further to 300 and the pressure to 110 p. s. i. g. to maintain 265° C. After that, conditions were varied frequently to study a number of variables.

Steady reaction conditions prevailed as long as the recycling rate of oil was constant, but the system was quite sensitive to changes. Owing to mechanical failures of the oil pump, runaway temperatures were observed seven times during this run. These high temperatures caused carbon formation and quickly lowered the activity of the catalyst.

NONEVAPORATIVE COOLING

As operating temperature and pressure had to be varied simultaneously in experiment 10, the effect of each could not be observed independently. Furthermore, the temperature gradient across the bed varied with operating conditions. For these reasons an attempt was made in experiment 11 to evolve a method of operation whereby the heat of reaction would be dissipated as sensible heat of the coolant oil. The first 3 days on stream were devoted to establishing a minimum operating pressure at which comparatively wide variations of temperature were possible. During this time the pressure was increased in increments until, at a pressure of about 150 p. s. i. g. and an hourly space velocity of 100, the temperature could be controlled independently of pressure. Higher pressures and gas rates could also be used at any desired temperature. The flow rate of recycle oil controlled the temperature gradient across the catalyst bed. With the catalyst submerged no runaway temperatures occurred, and operation was considerably smoother than in the previous experiment. This mode of cooling was therefore adopted for all subsequent submerged-bed experiments.

Typical conditions for fixed-bed operation (from experiment 17-B) were: An hourly space velocity of fresh gas of 300 (123 S. T. P. cu. ft. per hr. per 0.41 cu. ft. of catalyst); pressure, 300 p. s. i. g.; gas-recycle ratio, 1 : 1; oil flow, 50 gal. per hr.; maximum temperature, 256° to 265° C.; and rise through the bed at 70-percent gas conversion, 15° C. A heat balance for 1 hour of such operation follows:

	B. t. u.	*Percent*
Heat liberated:		
(123) (0.70) cu. ft. × 72 B. t. u. per cu. ft.	6,200	100
Heat absorbed:		
(a) By circulating oil:		
(50 gal.) (6.5 lb. per gal.) (0.6 B. t. u. per lb.-° F.) (15° C.×1.8° F. per °C.)	5,300	85
(b) By gases:		
$[(205)(0.020)+35(0.04)+10(0.065)]\frac{\text{B. t. u.}}{\text{° F.}}(15\times1.8)$ °F. H_2+CO CO_2+H_2O C_1 to C_4	160	3
(c) As latent heat:		
(6 lb. of oil vaporized) (125 B. t. u. per pound)	750	12
Total	6,200	100

Thus, 85 to 90 percent of the heat of reaction was removed as sensible heat in the circulating oil. In large-scale operation virtually all of this heat could be recovered by conventional heat exchange and used to generate steam. On the other hand, heat of reaction removed by evaporative cooling (as latent heat) could not be recovered as efficiently owing to the presence of the permanent gases. Therefore, an economic advantage as well as considerably improved temperature control is gained by utilizing the principle of nonevaporative cooling.

INDUCTION

Since temperature was rendered independent of operating pressure by employing nonevaporative cooling in experiment 11, an improved method of catalyst induction was developed in experiment 12. The importance of induction of the catalyst to its activity and life had been stressed by many German investigators (*56*). The arbitrary induction used for experiment 12 was based on the assumption that better activity would result if temperature and conversion were increased gradually over a period of several days. After enough cooling oil had been added to the converter through which nitrogen was flowing, the rate of oil circulation was adjusted to the required value and the temperature adjusted at 150° C. Nitrogen was then replaced by synthesis gas flowing at an hourly space velocity of 300, based on the volume of the settled bed. After the system was purged of nitrogen, the pressure was increased to 300 p. s. i. g. During the induction the temperature was steadily raised from 150° to about 230° C., where 30 percent of the synthesis gas was converted. This temperature was maintained for 24 hours. The conversion was then raised further by increasing the temperature and maintained for 24 hours at 45 percent. Similarly, it was maintained at 60 percent for the next 24 hours. On and after the fourth day 70-percent conversion was obtained. A summary of the induction procedure is:

Date, March 1948	H_2+CO conversion, volume-percent	Maximum temperature, °C.	Temperature differential, °C.
4	29.6	232	14
5	44.1	256	18
6	62.1	272	21
7	70.8	285	19

Apparently as a result of the change in induction procedure, catalyst activity in experiment 12 improved significantly over experiment 11. Specifically, operating temperature was lowered by 10° to 20° C. In an effort to improve performance to an even greater degree, further modifications in induction were made in experiment 13. With gas flowing at an hourly space velocity of 100, the temperature was gradually increased to 250° C. over a 2-day period to reach a conversion of 70 percent. After 24 hours the hourly space velocity was increased to 200, held for a few hours, and finally increased to 300. Even though the maximum temperature reached 305° C., 70-percent conversion was not attained. This method of induction was therefore abandoned. The stepwise method described for experiment 12 was used to induct the fresh catalysts in all of the remaining fixed-bed experiments.

SYNTHESIS

Following induction, synthesis was carried out so as to obtain conversion of 70 percent of the synthesis gas. For experiments 10 through 16, $1H_2+1CO$ gas was used and for experiment 17, $1.3H_2+1CO$. An active catalyst required an increase in temperature of 1° or 2° C. per week to maintain constant conversion. As the catalyst aged and temperatures were increased, the usage ratio declined, and proportionally more carbon monoxide was consumed, so that the $H_2:CO$ ratio in the exit gas increased. This condition is undesirable, because it is difficult to attain high conversion of synthesis gas of such composition in multistage operation where the exit gas from one converter is to be used as the feed gas in the next. Moreover, a hydrogen-rich synthesis gas produces greater amounts of undesirable C_1 plus C_2 gases.

GAS RECYCLE

To make the usage ratio agree closely with the composition of the fresh gas, a portion of the tail gas, from which water had been largely removed by cooling to 5° C. at synthesis pressure, was recycled starting with experiment 14–A. By this means the partial pressure of water was reduced, and the amount of carbon monoxide converted to carbon dioxide by the water-gas shift, $H_2O+CO \rightarrow H_2+CO_2$, was reduced substantially. Thus, variation of the recycle rate made possible a shift of the usage ratio within certain limits. In addition, recycling the gas improved the activity of the catalyst.

PROBLEM OF CATALYST AGGLOMERATION

A major difficulty encountered in this series of experiments (12 to 17) was gradual increase of pressure differential through the catalyst bed during synthesis. This change was caused by agglomeration that interfered with the flow of gas and oil and eventually stopped the experiments. Some tendency toward lower conversion usually accompanied this plugging, and the temperature had to be raised to maintain the desired conversion. At the end of all of these experiments, each of which was operated 1 month or longer, the catalyst was cemented together so firmly that it had to be chiseled out of the converter. Heavy deposition of carbon occurred on and between the catalyst particles throughout the bed, as evidenced from the fact that chemical analyses of the cementing material showed its free carbon content to be 10 to 18 weight-percent. This condition was not due to hot spots because the temperature was controlled very precisely and the catalyst was always submerged in moving oil. However, the rate of formation and deposition of carbon, as indicated during operation by the measured pressure differential through the catalyst bed, were accelerated when high temperatures (285° to 305° C.) were employed (experiments 12, 13, 15).

Particles from a cemented catalyst (experiment 14) were still active, even though the activity apparently had dropped sharply during synthesis. This fact was established in a test made in a small, fixed-bed reactor with a sample of discharged catalyst (experiment 14–C). Before this test the catalyst was extracted with toluene and screened to remove the fines and to separate the 4- to 6-mesh fraction. Although the activity had seemed to drop during experiment 14–B, the activity of this extracted sample was actually equivalent to that obtained initially in experiment 14–A. The sample performed satisfactorily in the fixed bed for an additional 2,400 hours, a total of 4,707 hours of synthesis. Thus, some physical phenomenon associated with cementation, such as filling of the void space with carbon, caused the decline in activity observed in experiments 12 to 17. For this reason a serious effort was made to avoid, or at least minimize, the occurrence of cementation.

Presence of Acids.—A certain amount of oxygenated compounds, including organic acids, was formed in all experiments. The acids are suspected as adversely affecting the physical strength and chemical activity of the catalyst. In most instances, when the cooling oil became dark and its iron content was increased (indicating disintegration of catalyst), the acid number of the products also rose to a marked degree. However, the acid number sometimes rose, even when the amount of iron in the recycle oil remained low. The increased resistance to flow through the bed was also associated with the presence of acid when a large pressure drop developed in experiment 14–C. This test followed a period (14–B) during which the acidity of light oil and aqueous material had been high enough to corrode the steel pipe just below the overhead condenser.

When a sample of unused, reduced iron catalyst was placed in oil to which enough glacial acetic acid had been added to give an acid number[9] of 10 mg. potassium hydroxide per gram of oil and the sample was warmed slightly, the catalyst froze to a rigid mass within 5 minutes. A mixture of propionic acid and oil having an acid number of 10, and a light product oil (from experiment 14–C) with an acid number of 30 acted similarly. An additional test made with pelargonic acid ($C_8H_{17}COOH$), boiling point 253° to 254° C., demonstrated that higher acids in the circulating oil affected reduced catalyst similarly.

Because of these observations, several attempts were made to reduce the acid content of the cooling oil. In experiments 14 C, 15 A, and 16–A the overhead condenser was operated "hot" (100° to 115° C.) rather than "cold" (45° C.), because it was thought that elimination of reflux would allow the overhead product, containing most of the acid, to be removed completely and continuously, thus reducing the acid content of the circulating oil. Furthermore, the feed oil for these experiments was neutralized by treating it with an aqueous caustic wash, followed by a water wash to remove the sodium salt. In a more direct approach, several charges of alcoholic sodium hydroxide were injected into the recycle oil during experiment 15. Despite these efforts, cementation was not prevented, and the acid content of the circulating oil remained essentially unchanged. Consequently, these procedures were abandoned.

Use of 2- to 4-Mesh Catalyst.—Another attempt to prevent or at least delay cementation was made by using larger (2- to 4-mesh) catalyst particles with greater void volume in experiment 16–A. This catalyst was reduced and inducted in the same manner employed in experiments 14 and 15 and used under similar operating conditions; that is, hourly space velocity of 300, $1H_2+1CO$ synthesis gas, 2:1 gas recycle, and 70-percent conversion at 300 p. s. i. g. To achieve 70-percent conversion, an initial temperature of 272° C. was required, about 18° C. higher than in experiment 14–A and 13° C. higher than in experiment 15–A. The initial pressure drop across the catalyst bed was only 2 p. s. i. compared with 5 to 6 p. s. i. for experiments 14 A and 15–A; other operating conditions were the same. After 38 days of operation the pressure drop had increased to only 9 p. s. i. compared with 30 p. s. i. in experiment 15–A after the same time of operation. Thus, larger size of the catalyst particles effected a delay in the rate at which pressure drop developed but did not prevent cementation.

REACTIVATION

When the observed activity had declined appreciably after 2,000 hours of synthesis in experiment 14–B, the catalyst was reactivated to avoid replacement, which for large-scale operation would be costly. The oil was drained from the converter; the catalyst was extracted with toluene and then treated with hydrogen in place at atmospheric pressure, temperature about 450° C., and an hourly space velocity of 100. Other investigators had reported that this method of treatment, given at intervals, was effective in restoring cobalt and iron to satisfactory activity (*44*). Considerable amounts of methane, water, and carbon dioxide were evolved, indicating decomposition of retained organic materials and/or iron carbide and reduction of magnetite to metallic iron. The treatment was terminated after 7 days when the composition of the exit gas approximated that of the incoming hydrogen. Upon resumption of synthesis, 70-percent conversion was attained at 5° to 10° C. lower temperature than before the treatment. Even though the activity was improved, this method was undesirable because it involved draining the oil from the converter and required a relatively high temperature for reduction.

To determine whether the catalyst might be reactivated at temperatures not destructive to the oil, a special test was made in a small, dry-bed reactor at 275° C. with hydrogen under 300 p. s. i. g. pressure. An extracted 4- to 6-mesh sample of discharged catalyst from experiment 14–C was used. The treatment effected substantially complete decomposition of iron carbide with an almost identical increase of metallic iron:

	Weight-percent	
	Before treatment	*After treatment*
Total Fe	77.0	82.1
Total C	10.8	4.21
Metallic Fe	19.7	60.2
Fe as carbide	41.1	2.51
Fe not accounted for	[1] 16.2	[2] 19.4

[1] Probably mostly magnetite.
[2] Probably some magnetite.

On the basis of this test, similar reactivation treatment was given the submerged catalyst in experiment 17. Although not as effective as treatment at high temperature (450° to 500° C.), this reactivation retarded the decline in activity and was adopted as a standard procedure thereafter.

USE OF HYDROGEN-RICH GAS

It was believed that hydrogen-rich gas would lower the rates of formation of carbon and acid and thus increase the life of the catalyst; so $1.3H_2+1CO$ (instead of $1H_2+1CO$) was used in experiment 17. To assist further in maintaining a fairly high partial pressure of hydrogen

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[9] Determined by ASTM Procedure D663-44T.

in the tail gas, the recycle-gas ratio was adjusted to 1 so that the usage ratio was about 1.1:1. Other conditions were similar to those for experiments 14, 15, and 16: Hourly space velocity of fresh gas 300, pressure 300 p. s. i. g., and conversion 70 percent.

In several important respects the results of this operation were more satisfactory than the experiments with $1H_2+1CO$ gas. The pressure drop across the bed increased from an initial value of 4 p. s. i. to a maximum of 15 p. s. i. in 2,360 hours, more than twice the time required in previous experiments. When the run was terminated voluntarily, the catalyst was still active, with 265° C. sufficing for 70-percent conversion. A 10° C. increase had been required to maintain constant conversion during this period, which was good performance for iron catalysts throughout this work. Even with the hydrogen-rich gas the specific yield of C_1 plus C_2 was the same (about 35 gm. per m.³) as obtained with $1H_2+1CO$ at similar temperatures.

Although cementation occurred at a slower rate, it was not prevented, as evidenced by eventual development of appreciable pressure gradient. The catalyst was removed easily from the 2-foot space at the bottom of the converter, but the remainder (about 8 feet) was agglomerated and had to be chiseled and drilled out as in the earlier experiments. The apparently unavoidable recurrence of this difficulty led to adoption of the so-called "expanded-bed technique."

ADDITION OF CARBON DIOXIDE TO FRESH GAS

From March 16 to 24, 1949, during experiment 16, several tests were made in which approximately 12 percent of carbon dioxide was added to the fresh $1H_2+1CO$ synthesis gas. In 1 test about 20 percent of carbon dioxide was added to simulate the gas made from pulverized coal, oxygen, and steam in a gas generator operated under pressure. The results from these tests are summarized in table 9. When carbon dioxide was added, the amount of carbon converted to products other than carbon dioxide exceeded the maximum amount calculated on the basis of fresh carbon monoxide consumed. Some of the added carbon dioxide must thus have been converted to hydrocarbons, probably after conversion to carbon monoxide:

$$CO_2+H_2 \rightarrow CO+H_2O.$$

Addition of carbon dioxide impaired the activity considerably. Conversion of carbon monoxide and synthesis gas decreased, the latter from approximately 51 to 34 percent at the same operating temperatures (maximum 278° C., ΔT—13° C.). Hence, the use of such feed gases is not desirable with fused iron.

RESULTS AND DISCUSSION

Although the activity of the catalyst was unsatisfactory in experiment 11, this run did demonstrate the advantage of operation at higher pressures. The heat of reaction was removed by the cooling oil mainly as sensible heat rather than latent heat of vaporization, making temperature control independent of pressure. A pressure of about 150 p. s. i. g. was possible at an hourly space velocity of fresh gas of 100 and about 250 p. s. i. g. at an hourly space velocity of 300.

The data obtained in experiment 11 are summarized in table 10. When the pressure was increased from 135 to 190 p. s. i. g. (periods 1 through 3) while a constant hourly space velocity of 100 and a maximum temperature of 276° C. were maintained, conversion of gas rose from 53.4 to 76.8 percent, and the calculated space-time yield of C_3+ material increased from 172 to 246 kg. per m.³ of catalyst per day. A further increase of pressure to 252 p. s. i. g. (in period 4) made it possible to lower the temperature to 264° C. and still obtain 77-percent conversion. An increase in the usage ratio from 0.64 to 0.76 also accompanied the increase in

TABLE 9.—*Effect of addition of carbon dioxide on synthesis with fused iron in experiment 16–A*

[Mode of operation, submerged, fixed-bed; catalyst D 3004; range of mesh sizes, 2–4; ratio in fresh gas, H_2:CO 1, 1:1; S. V. H. settled bed, 300]

Test	1	1	2	2	3	3	4	4	5	5
Duration ..... hr.	14	17.5	15	6	5	2	2	2	2	2
Synthesis gas:										
CO_2 added ..... vol. percent.	—	10.7	—	10.9	—	10.8	—	18.7	—	9.2
Carbon consumed¹ ..... lb. atoms per hr.	0.0770	0.0617	0.0[illegible]8	0.0467	0.0092	0.0622	0.0039	0.0608	0.1028	0.1044
Conversion, vol. percent:										
CO	55.6	61.1	62.5	61.5	55.1	60.3	63.9	47.0	61.3	5[illegible].3
H_2+CO	51.4	45.9	57.8	54.9	57.4	38.4	61.7	49.1	33.7	29.4
Usage ratio, H_2:CO	0.806	0.86	0.829	0.962	0.844	0.796	0.842	0.522	0.573	0.877
Gas-recycle ratio	3.0	3.1	2.0	2.5	2.45	2.2	2.9	2.1	2.0	2.2
Pressure, average ..... p. s. i. g.	300									
Temperature, ° C.:										
Maximum	272	276	285	285	295	295	296	280	278	279
Differential	14	13	14	14	10	19	15	15	18	18

¹ For products exclusive of carbon dioxide.

TABLE 10.—*Summary of data for experiment 11–A*

[Duration, 8–10 hr.; mode of operation, cocurrent, expanded-bed; catalyst No., [illegible]; range of mesh sizes, 4–6.]

Equilibrium period	1	2	3	4	5	6
Oil, recycle rate, gal./hr.	8	15	15	15	20	30–40
Synthesis gas:						
S. V. H. (settled bed)	100	100	100	100	200	300
Conversion, vol.-percent:						
CO	64.8	75.5	88.3	88.3	87.8	82.5
H_2+CO	53.4	64.0	76.8	77.1	77.8	71.3
Usage ratio, H_2:CO	0.64	0.71	0.74	0.76	0.78	0.80
Pressure, maximum, p. s. i. g.	135	150	190	252	259	268
Temperature, ° C.:						
Maximum	275	276	276	284	283	297
Differential	23	16	18	20	24	20
Yields:						
Specific, gm./m.³ C_3+	58.3	61.1	61.4	(1)	66.2	72.0
Space-time, of C_3+—kg./m.³ settled cat. vol./day, calculated	172	212	245	(1)	487	623

[1] No gas sample.

pressure, revealing another important advantage of increased operating pressure.

At the highest hourly space velocity (300 in period 6) an increase in the recycling rate to about 35 to 40 gal. per hr. of oil was adequate to control the temperature differential in the catalyst bed. An operating temperature of nearly 300° C. was possible at a converter pressure of 268 p. s. i. g. Even at this high temperature, which usually would affect the H_2:CO usage ratio adversely, this ratio increased to 0.80:1, and the space-time yield of liquid hydrocarbons was the highest that had been obtained during this investigation.

Operational conditions and selected data from experiments 12 to 17 are summarized in tables 11 and 12. Product data are also shown in table 12. At the start of these tests, the catalysts were 90- to 95-percent reduced. Except for a brief induction period during experiment 13 A, the hourly space velocity of synthesis gas was maintained at 300 throughout this series. To achieve 70-percent conversion of the gas, temperatures of 250° to 285° C. were initially required after stepwise activation.

Recycling of tail gas (beginning with experiment 14) improved the activity of the catalyst and also the usage ratio that tended to remain lower than the H_2:CO ratio in the feed gas, especially at higher temperatures and with older catalysts.

Catalyst agglomeration was still encountered throughout this series. Changes in operation, such as a "hot" rather than a "cold" condenser, use of an acid-free feed oil, and direct caustic injections into the recycled coolant oil, failed to solve this problem or even appreciably lengthen operating time before enforced shutdown. The use of larger (2- to 4-mesh) particles in experiment 16 reduced the rate of increase in pressure drop across the catalyst bed (table 12). However, the catalyst eventually cemented, so that the test had to be stopped. In addition, the initial activity of the larger particles was poorer, probably because the 4- to 6-mesh catalyst had about 72 percent more area. As a matter of fact, the lower activity more than overbalanced any advantage accruing from lower pressure drop.

Operation with a hydrogen-rich ($1.3H_2+1CO$) gas in experiment 17 was very satisfactory. The initial catalytic activity was comparable with that of the most successful run with $1H_2+1CO$ (experiment 14), and the activity remained quite stable. An increase of about 1° C. per week was sufficient to maintain 70-percent conversion. Cementation was much less rapid than previously. After about 2,000 hours of synthesis, the pressure differential had increased from 3 to 15 p. s. i. compared with about 49 p. s. i. in experiment 14 during a similar period. There was no apparent shift in distribution of products attributable to temperature in experiments 14 to 17, although proportionately higher yields of light products are usually associated with operation at higher temperatures (*44*).

PRODUCTS

To explain the manner in which the products from the fixed-bed experiments were evaluated, detailed product information will be presented for a period of operation from experiment 17–B (table 12, catalyst age 1,524 to 2,148 hours), in which $1.3H_2+1CO$ was used at an hourly space velocity of 300 with 70-percent conversion, 1:1 gas-recycle ratio, and 300 p. s. i. g. pressure.

COLLECTION

The liquids collected from the system, shown in figure 8, were charcoal spirits (*1*), light oil (*2*), reflux oil (*3*), heavy oil (*4*), and an aqueous layer (*5*), which contained most of the water-soluble organic oxygenated compounds. The charcoal spirits was that portion of the light oil that was recovered from the activated charcoal by steam stripping and refrigeration at about 5° to 10° C. Reflux oil was not considered to be a product but was examined only to control the properties of the oil in the converter. Total daily yields are given in table 13.

The measured gases (fig. 8) were fresh synthesis gas (*A*), mixed gas (*B*), recycle (C_1) and tail gas (C_2) which were identical in composition, exit gas (*D*), and the charcoal-sorbed gases (*E*). The volumes, and compositions of these streams determined by mass spectrometer are given in table 14, which also contains calculated daily recoveries of compounds C_1 through C_6.

CHARACTERIZATION

Analyses of typical liquid samples obtained in experiment 17–B are given in table 15. ASTM distillations were carried out with the light and reflux oils. A simple vacuum distillation was made on the heavy oil, and the temperatures were corrected to atmospheric pressure. An approximate product distribution (table 16) was computed from this information. Some difference between these figures and the

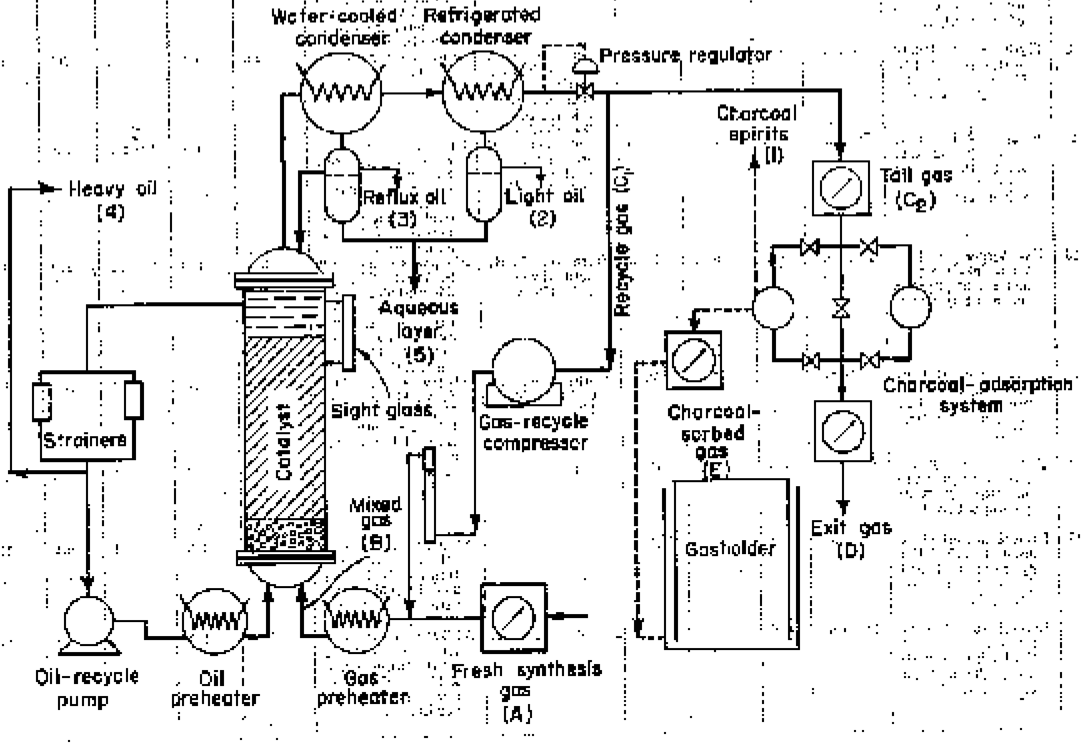

FIGURE 8.—Submerged, Fixed-Bed Unit, Showing Product Streams.

TABLE 11.—*Summary*

Experiment No.	Main purpose	Catalyst[1]		Iron charged, lb.	Catalyst reduction, percent	Initial cooling oil	Catalyst induction	Synthesis				
								Gas			Initial conditions	
								S. V. H. of fresh synthesis gas	Fresh gas ratio, H_2:CO	Recycle gas ratio	Temperature, ° C.	
		No.	Mesh								Maximum	Differential
12	Remove heat of reaction mainly as sensible heat rather than by vaporization of cooling oil.	D-3001	4-6	65.5	[2] 89.7	Primol "D" (lubricating oil), b. 200°-400° C.	Stepwise at 300 S. V. H., 25-, 40-, 65-, and 85-percent CO_2-free contraction.	300	1.0	--------	283	19
13	Simulate tail-gas recycling by adding CO_2 to synthesis gas; study diluent effect of CO_2.	D-3001	4-6	60.5	[2] 92.6	do.	Started at 100 S. V. H., temp. raised to attain 70-percent conversion, then S. V. H. raised to 300 and temp. again increased.	100 300	1.0 1.0	-------- --------	248 249	17 17
14-A	Study effect of gas recycling; achieve better usage ratio.	D-3006	4-6	42.8	[3] 94.2	Humble diesel oil, b. 250°-300° C.	Stepwise at 300 S. V. H., 25-, 40-, 65-, and 85-percent CO_2-free contraction, 2:1 gas recycle.	300	1.0	2	265	17
14-B	Continuation of experiment 14-A after deliberate interruption to test life of catalyst.	D-3006	4-6	--------	--------	From exper. 14-A, b. 260°-375° C.	At 300 S. V. H. and 2:1 gas recycle, temp. increased rapidly to obtain 75-percent conversion in 24 hr.	300	1.0	1.8-2.25	265	10
14-C	Hydrogen treatment of dry bed at 400° C. for 7 days to reactivate catalyst.	D-3006[4]	4-6	--------	[5] 10.7	From exper. 14-A and 14-B, neutralized by washing with alkali, b. 300°-390° C.	Same as for exper. 14-A.	300	1.0	1	261	10
15	Reduce acid content of circulating oil to retard increase in pressure across catalyst bed.	D-3006	4-6	43.2	92.0	From exper. 14-B and 14-C, neutralized, b. 300°-450° C.	Stepwise at 300 S. V. H., 25-, 40-, 65-, and 85-percent CO_2-free contraction, 2:1 gas recycle started at 25-percent CO_2-free contraction.	300	1.0	2.0-2.5	254	16
16	Use larger catalyst particles to retard increase in pressure across catalyst bed.	D-3006	2-4	46.2	93.5	From exper. 14-B, neutralized, b. 250°-450° C.	Stepwise at 300 S. V. H., 25-, 40-, 65-, and 85-percent CO_2-free contraction, 2:1 gas recycle started at 85-percent CO_2-free contraction.	300	1.0	2.0-2.2	272	18
17-A	Avoid cementation of catalyst and pressure buildup by use of 1.3H_2:1CO.	D-3006	4-6	47.4	95.5	From exper. 14 to 16, b. 300°-450° C.	Stepwise at 300 S. V. H., 25-, 40-, 65-, and 85-percent CO_2-free contraction, 1:1 gas recycle.	300	1.3	1	250	16
17-B	Prolong catalyst life and retard pressure buildup by rereducing catalyst.	D-3006	4-6	--------	[5] 86.4	do.	do.	300	1.3	1	256	15
17-C	Investigate effect of low-temp. (265° C.) hydrogen treatment (40 hr.) on used catalyst.	D-3006	4-6	--------	[5] 27.7	do.	At 300 S. V. H. and 1:1 gas recycle, temp. raised from 246° to 255° C. at rate of 2°-3° C. per hr.	300	1.3	1	264	15
17-D	Investigate effect of low-temp. (265° C.) hydrogen treatment (80 hr.) on used catalyst.	D-3006	4-6	--------	[6] 40.7	do.	At 300 S. V. H. and 1:1 gas recycle, temp. raised from 250° to 255° C. at rate of 2°-3° C. per hr.	300	1.3	1	265	14

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[1] Fixed bed, 3 ft. deep, 0.411 cu. ft. settled volume.

[2] Reduced in place.

[3] Reduced in separate unit, as were all raw catalysts thereafter.

[4] Settled volume only 0.350 cu. ft.

[5] Extent of reduction corresponding to amount of water evolved during treatment.

[6] Catalyst was given low-temperature (275° C.) treatment in place under oil followed by treatment at higher temperature (420° C. average) in dry bed. Before these treatments catalyst was only 19.6 percent reduced.

of experiments 18 to 17

Synthesis—Continued												
Initial conditions—Continued				Final conditions						Duration, hr.	General comments	Special operations
Pressure		H2+CO conversion, vol.-percent	Usage ratio	Temperature, °C.		Pressure		H2+CO conversion, vol.-percent	Usage ratio			
Maximum, p. s. i. g.	Differential, p. s. i.			Maximum	Differential	Maximum, p. s. i. g.	Differential, p. s. i.					
259	3	70.8	0.72	265	56	310	15	61.0	0.67	600	Temperature control improved; capacity of pump inadequate for controlling differential temperature.	Charcoal recovery.
207 306	2 3	71.4 62.9	.60 .90	306	45	320	42	45.0	.35	336	Rapid increase of differential pressure causing inoperable conditions; poor activity; original purpose not accomplished.	None.
320	5	70.0	1.04	250	16	327	10	70.0	.98	1,200	Smooth operation; only small differential pressure increase; good activity.	None.
303	12	69.0	.91	269	20	308	42	58.0	.87	700	Rapid increase of differential pressure caused inoperable conditions.	None.
320	45	65.7	.96	263	26	317	44	49.5	.74	316	Activity slightly improved by hydrogen treatment; high differential pressure forced elimination of gas recycling.	Reflux condenser operated "hot" and "cold" to study effects of acid in circulating oil.
301	5	70.0	1.08	264	15	310	35	48.0	.91	940	Satisfactory initial activity; acid concentration not reduced; recurrence of high differential pressure caused rapid loss of conversion.	"Hot" condenser used; feed oil neutralized; alcoholic caustic added directly to circulating oil.
301	2	70.0	1.00	376	15	306	9	52.0	.92	535	Less active than 4- to 6-mesh; less building of differential pressure, but cementation occurred.	Condenser operated "hot" and "cold"; feed gases with 12 and 20 vol.-percent CO2 used for dilution study.
307	3	68.3	1.14	262	16	305	5	62.9	1.14	843	Activity comparable with expt. 14; only small differential pressure increase; good activity.	Charcoal recovery.
298	0	72.1	1.10	245	15	322	15	68.4	1.05	1,517	Satisfactory operation; only relatively small differential pressure increase; good activity; terminated voluntarily.	Recycle-gas ratio raised from 1 to 2 to 3 to observe effect on C3+C4 yield and usage ratio.
290	7	70.3	1.11	265	14	310	16	65.0	1.01	96	No improvement of activity.	None.
306	13	71.1	1.19	263	14	302	11	70.5	1.24	104	Slight improvement of activity.	None.

TABLE 12.—*Summary of typical operating data for fixed-bed experiments 12 to 17*

[Mode of operation, submerged, fixed-bed; height of catalyst (settled) 3 ft.]

Experiment No.	12	14-A	14-B	15-A	16-A	17-A	17-B	17-B
Catalyst:								
Number	D-3001	D-3006	D-3008	D-3035	D-3008	D-3006	D-3005	D-3006
Total age, hr.	500	3,300	3,800	650	875	2,360	2,350	2,480
Age for period, hr.	350-480	630-770	1,300-1,540	250-800	218-319	264-344	785-1,251	1,624-2,148
Range of mesh sizes	4-6	4-6	4-6	4-5	3-4	4-6	4-5	4-6
Oil:								
Fresh makeup, boiling range at 1 atm., ° C.		250-330	200-340	300-460	200-400	300-400		
Lb./day	0.0	9.57	0.62	16.61	11.21	0.48	0.0	0.0
Synthesis gas:								
Ratio in fresh gas, H_2:CO	0.99	1.01	1.03	0.97	0.97	1.30	1.33	1.31
S. V. H. (settled bed)	300	300	302	300	300	302	302	311
Flow, cu. ft. per hr. (S. T. P.)	130.5	124.1	121.7	126.1	123.5	124.0	124.9	153.7
Space-weight velocity of H_2+CO cu. ft. (S. T. P.) per hr. per lb. Fe	1.82	2.57	2.36	2.46	2.47	2.60	2.61	2.60
Conversion, vol.-percent:								
CO	82.8	81.3	72.7	74.8	69.4	71.6	76.3	80.6
H_2	57.5	70.7	67.3	64.9	68.1	64.4	65.5	65.7
H_2+CO	70.6	70.4	69.9	60.0	68.7	67.6	70.9	70.0
Space-weight conversion cu. ft. (H_2+CO) (S. T. P.) per hr. per lb. Fe	1.20	2.01	1.90	1.68	1.68	1.78	1.86	1.82
Usage ratio, H_2:CO	0.88	1.08	0.95	0.94	0.98	1.17	1.13	1.01
Gas-recycle ratio	None	2	2	1	1	1	1	1
Pressure:								
Maximum, p. s. i. g.	304	302	274	300	303	300	308	377
Differential, p. s. i.:								
Start of experiment	5	5	12	8	2	3	5	5
End of experiment	15	30	49	36	9	6	16	15
Temperature, ° C.:								
Maximum	283	252-258	244-250	270-276	273	260-265	250-255	257-265
Differential	19	17	18	18	12	15	15	15
Yields:								
Specific, gm. per m.³:								
CH_4	12.7	22.2	17.8	20.1	19.5	45.2	18.0	18.6
C_2H_6	6.0	14.7	12.1	9.5	10.0	12.2	11.2	10.9
C_2H_4	0.2	2.5	3.4	5.4	2.4	3.5	3.6	4.1
C_3H_8	3.3	3.9	7.4	2.5	0.7	6.9	7.7	5.7
C_3H_6	22.2	12.9	14.8	16.2	17.4	37.7	19.0	13.7
C_4H_{10}	3.0	4.7	0.8	3.7	2.2	7.5	5.8	4.3
C_4H_8	14.2	11.0	16.9	9.3	12.7	18.8	12.4	10.4
C_5H_{12}	0.7	1.1	1.9	1.5	0.8	2.2	3.1	1.7
C_5H_{10}	0.8	5.5	5.5	4.7	3.7	6.4	7.3	6.3
C_6H_{14}							0.2	1.3
C_6H_{12}				0.0	0.4			2.7
C_7H_{16}							3.4	3.4
C_1+, total	173.0	142.5	151.3	150.5	146.2	146.2	159.6	146.3
Space-time of C_5+, kg. per m.³ settled-cat. vol. per day:								
Actual	890	718	740	754	773	700	579	747
Calculated	632	861	855	847	856	644	554	870
Products:								
Recovery, lb. per day:[2]								
Heavy oil	3.06	6.30	7.82	7.40	4.90	5.03	6.54	7.20
Light oil	11.88	13.47	7.14	13.10	13.05	5.12	4.94	5.22
Reflux oil	2.74	2.71	6.74	2.90	4.32	2.02	1.10	1.08
Charcoal spirits and gas	2.74						0.45	0.45
Aqueous layer	5.01	14.75	12.63	10.83	19.69	18.01	18.20	13.97
Distribution of C_5+, lb. per day:[3]								
Gasoline (C_5—		13.17	21.54	11.88	11.85	11.61	14.05	12.20
Diesel oil		2.10	3.18	1.44	1.67	2.58	2.51	2.43
Heavy distillate		1.48	1.67	2.36	3.05	1.92	2.08	2.50
Wax		1.65	2.40	2.01	2.14	1.86	1.34	1.82
Distribution of C_5+, wt.-percent:[4]								
Gasoline (C_5—		71.8	61.6	58.7	64.0	65.0	48.9	63.3
Diesel oil		11.4	17.0	12.3	9.0	14.5	20.0	12.6
Heavy distillate		8.0	8.4	13.3	15.4	10.6	12.8	14.6
Wax		8.8	12.8	14.5	11.6	10.2	8.3	9.5
Material balance, percent recovery	95.0	95.4	96.5	91.2	98.7	94.3	95.8	97.5

[1] C_1–C_4 material only; C_5–C_6 included in specific yields given.

[2] Net recoveries exclusive of feed oil, including oil-soluble oxygenates.

[3] Including oil-soluble oxygenates.

[4] Excluding oil-soluble oxygenates.

TABLE 13.—*Yields from experiment 17–B*

Product:	Yield, lb. per day
Gases:	
C_1–C_2	4.61
C_3–C_4	4.65
C_5–C_6	1.55
Oils:	
Heavy	7.20
Light	5.22
Reflux	1.08
C_5+ from charcoal spirits[1]	.45
Aqueous layer:	
Oxygenates	2.39
Water	11.58

[1] C_1–C_4 material only. C_5 C from charcoal recovery is included in gas yields.

true values may be expected because of the presence in the oils of small amounts of oxygenated compounds distilling as azeotropes with the hydrocarbons. In compiling table 16 an effort was made to correct for oxygenated compounds by subtracting the amounts of alcohols, acids, esters, ketones, and aldehydes found in the several crude product fractions by infrared examination. Nominally at least, this procedure should give the amount of oxygen-free products, except for handling and processing losses.

Fuel ratings of some samples are given in

TABLE 14.—*Analyses of gas streams from experiment 17–B*

Streams in fig. 8	(A) Fresh feed (2,970 cu. ft. per day)		(B) Inlet gas (5,940 cu. ft. per day)		(C) Recycle gas (2,970 cu. ft. per day)		(C₁) Tail gas (1,387 cu. ft. per day)			(D) Exit gas (1,246 cu. ft. per day)			(E) plus (I) combined; charcoal recovery (41.0 cu. ft. per day)		
Component	Vol.-percent	Lb. per day	Vol.-percent	Lb. per day	Vol.-percent	Lb. per day	Vol.-percent	Lb. per day	Gm. per m.³ of feed gas	Vol.-percent	Lb. per day	Gm. per m.³ of feed gas	Vol.-percent	Lb. per day	Gm. per m.³ of feed gas
CO_2	0.2	0.70	13.86	98.2	26.68	57.5	26.66	45.5	245.5	26.17	43.6	234.0	41.55	2.1	
CO	43.0	94.7	30.57	140.9	17.74	41.8	17.75	19.2		18.78	16.2				
H_2	56.6	9.4	51.34	17.1	46.12	7.7	46.13	3.6		47.9	5.8				
CH_4	.2	.27	2.25	6.02	4.32	6.76	4.32	2.57	18.0	4.45	2.67	15.0			
C_2H_6			.8	8.0	1.19	8.0	1.19	1.4	7.6	1.2	1.35	7.4	.98	.04	0.2
C_2H_4			.26	1.17	.61	1.17	.61	.56	2.0	.53	.55	1.9			
C_3H_8			.21	1.35	.43	1.65	.42	.73	4.0	.22	.08	2.9	3.48	.19	1.1
C_3H_6			.62	4.37	1.23	4.37	1.23	2.04	11.0	.89	1.69	8.6	9.23	.45	2.4
C_4H_{10}			.12	1.15	.25	1.16	.25	.55	3.0	.10	.17	.9	5.86	.38	2.1
C_4H_8			.51	2.56	.62	2.24	.62	1.35	7.2	.13	.26	1.4	14.85	1.67	4.9
C_5H_{12}			.04	.48	.08	.48	.08	.22	1.3				2.58	.22	1.2
C_5H_{10}			.16	1.74	.30	1.74	.3	.32	4.4				10.35	.82	4.4
C_6H_{14}			.02	.25	.06	.25	.06	.17	.2				1.71	.17	.9
C_6H_{12}			.06	.8	.11	.8	.11	.21	1.9				5.64	.24	1.8
N_2	.1	.22	.27	1.26	.44	1.08	.44	.54							
C_7+													3.06	.45	2.4

TABLE 15.—*Analyses of liquid products from experiment 17–B* [1]

Stream No. in fig. 8	(2)	(3)	(4)
	Light oil [2]	Reflux oil [2]	Heavy oil [3]
ASTM distillation, ° C.:			
First drop	43	74	207
5 vol.-percent	55	117	226
10 vol.-percent	60	135	247
20 vol.-percent	68	149	276
30 vol.-percent	77	158	310
40 vol.-percent	83	168	347
50 vol.-percent	92	173	385
60 vol.-percent	113	183	(4)
70 vol.-percent	126	191	
80 vol.-percent	140	202	
90 vol.-percent	161	219	
End point	198	250	
Gravity °API	64.5	54.6	42.0
Kinematic viscosity at 120° C. (248° F.) centistokes			2.73
Bromine No	77.4	43.3	22.7
Acid No	2.3	5.2	0.22

TABLE 16.—*Distribution of C_3+ products from experiment 17–B*

	Lb. per day [1]	Wt.-percent
Recovered gasoline, from charcoal spirits, reflux and light oil	9.32	
C_3+ in exit gas	2.78	
Total gasoline (C_3+)	12.10	63.2
Diesel oil	2.42	12.6
Heavy distillate	2.80	14.6
Wax	1.83	9.6
Total C_3+ production	19.15	100.0

[1] Values corrected for theoretical removal of oxygenates.

table 17. A motor octane rating of 37.0 was obtained with a sample of crude light oil that was distilled and cut at 190° C. in a 12-theoretical-plate column packed with steel helices. An ASTM distillation of this material showed its boiling range to be 50° to 195° C.; its bromine number was 67.8. A blend of 73.4 weight-percent of raw light oil and 26.6 percent of charcoal spirits had a motor octane rating of 64.3. This material was blended in the ratio in which the light oil and charcoal spirits were recovered. Actually, only about 60 percent of the C_3 to C_5 hydrocarbons in the tail gas is recovered by the charcoal traps. A higher octane value could therefore be obtained if the materials were mixed in proportion to their true production or if polymer gasoline was added in an amount equivalent to the unrecovered C_3 to C_5 components. The high quality of the diesel-oil cut (204° to 316° C.) is indicated by its cetane rating of 78.

TABLE 17.—*Fuel ratings of gasoline and diesel oil from experiment 17–B*

	Motor octane No. CFRM
Light oil (195° C. ASTM end point)	37.0
Light oil plus charcoal spirits (73.4:26.6 by weight)	64.3
	Cetane rating
Diesel oil	78.0

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[1] Catalyst age, 1,824 to 2,108 hr.
[2] ASTM distillation.
[3] Simple vacuum distillation at 1 mm. Hg absolute pressure; temperatures corrected to atmospheric pressure.
[4] 450 at 66 percent (35 percent wax under equilibrium conditions).