Making and Reducing Catalyst for Synthesis Operations

The catalyst fusion unit (see fig. 19) was described briefly in the 1950 Annual Report. The process for manufacturing synthetic ammonia-type fused iron oxide catalyst was novel in two respects. First, a commercial mill scale, economical and readily obtainable from steel rolling mills, was employed as the base material in place of magnetic iron oxide from the combustion of iron in oxygen, which had been used in the past. The mill scale was found to be pure enough for the purpose, although the ferrous:ferric iron ratio varied somewhat from a pure magnetic iron oxide. Secondly, the ferrous:ferric iron ratio was adjusted in the treatment, so that the proper ratio was obtained in the finished catalyst.

In 1951, 75,800 pounds of sized, unreduced catalyst was produced at a cost of $0.16 per pound. This cost does not include amortization of the plant but includes all other known elements of cost, such as materials, labor, utilities, and miscellaneous expense.

The catalyst-reduction unit was tested thoroughly in preliminary operations with sized sand approximating the size of the catalyst, and the apparent operational difficulties were determined and corrected. A total of 27,800 pounds of reduced catalyst was made.

Some difficulties were experienced in early operation of the catalyst-reduction unit. One of the most serious was deposition of carbon on screens and within the body of catalyst undergoing reduction. This was due to reduction of carbon-containing compounds in the hydrogen and was corrected by passing the heated hydrogen over a methanating catalyst before passage through the catalyst in the reduction vessel. A second serious difficulty was the channeling of catalyst in the reduction vessel. The reduction procedure was changed from continuous to batch operation, and from then on no further serious difficulties were experienced. The earliest catalyst processed in this operation was reduced to about 70 percent iron, while the balance was reduced to 85 to 95 percent.

Tests on the catalyst in bench-scale, pilot-plant, and demonstration-plant operations have shown this material to be as satisfactory as any other catalyst previously tested.

Fischer-Tropsch Synthesis and Distillation

Before the synthesis and distillation units were tested, several important changes were made. These included revisions to piping and equipment and correction of mechanical difficulties that affected the performance of several of the pumps and control instruments. In addition, insulation of exposed lines and equipment was completed.

In the synthesis unit the most important change adapted the synthesis reactor for "jiggling-bed" operation. Originally the synthesis reactor, 6 feet in diameter by approximately 30 feet over-all (see fig. 20), was designed for fixed-bed operation as an internally cooled converter. Because the "jiggling-bed" process requires the coolant oil and gas flows to be within defined linear

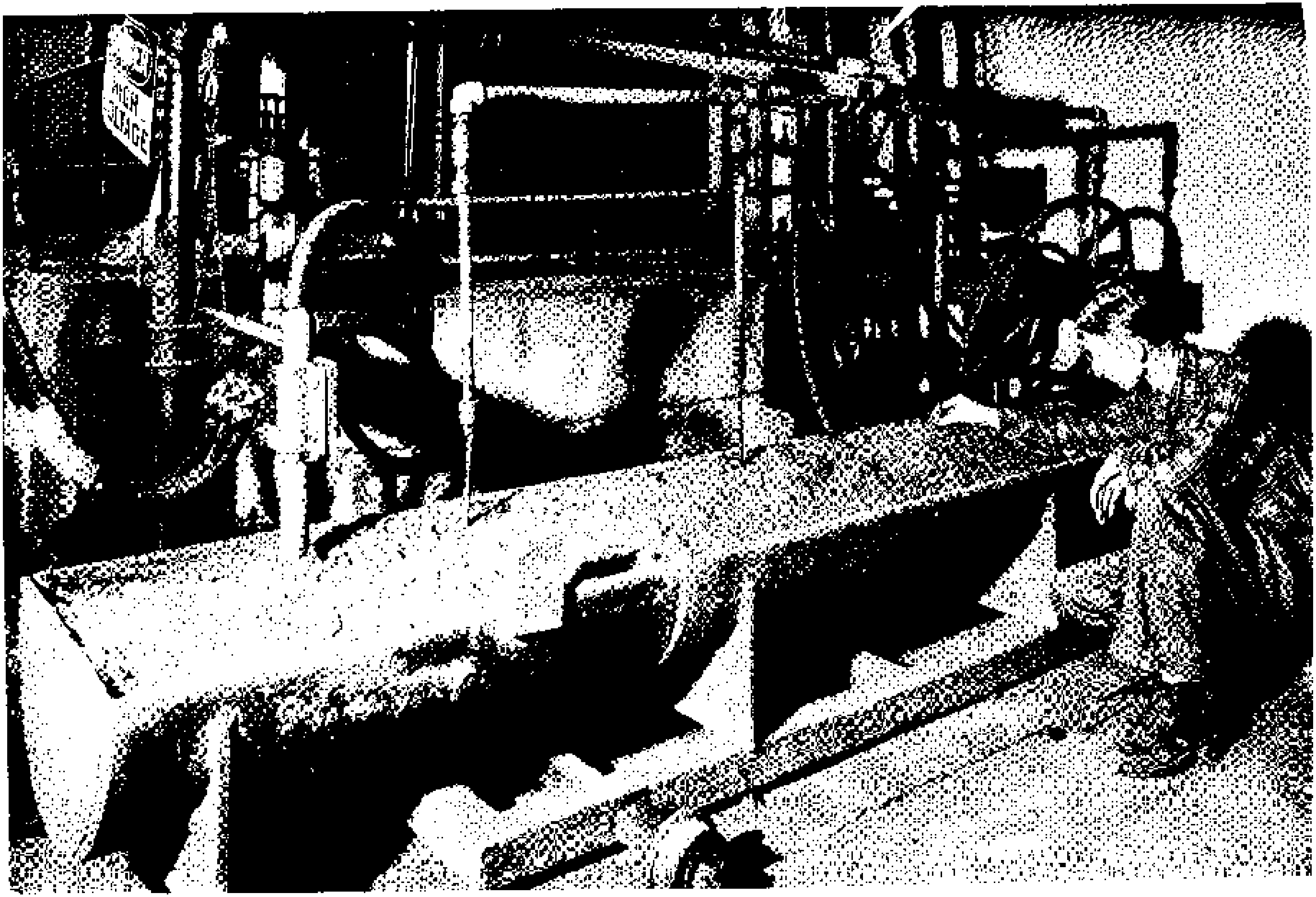

Figure 19 - Preparing to make Fischer-Tropsch synthesis catalyst by fusion method.

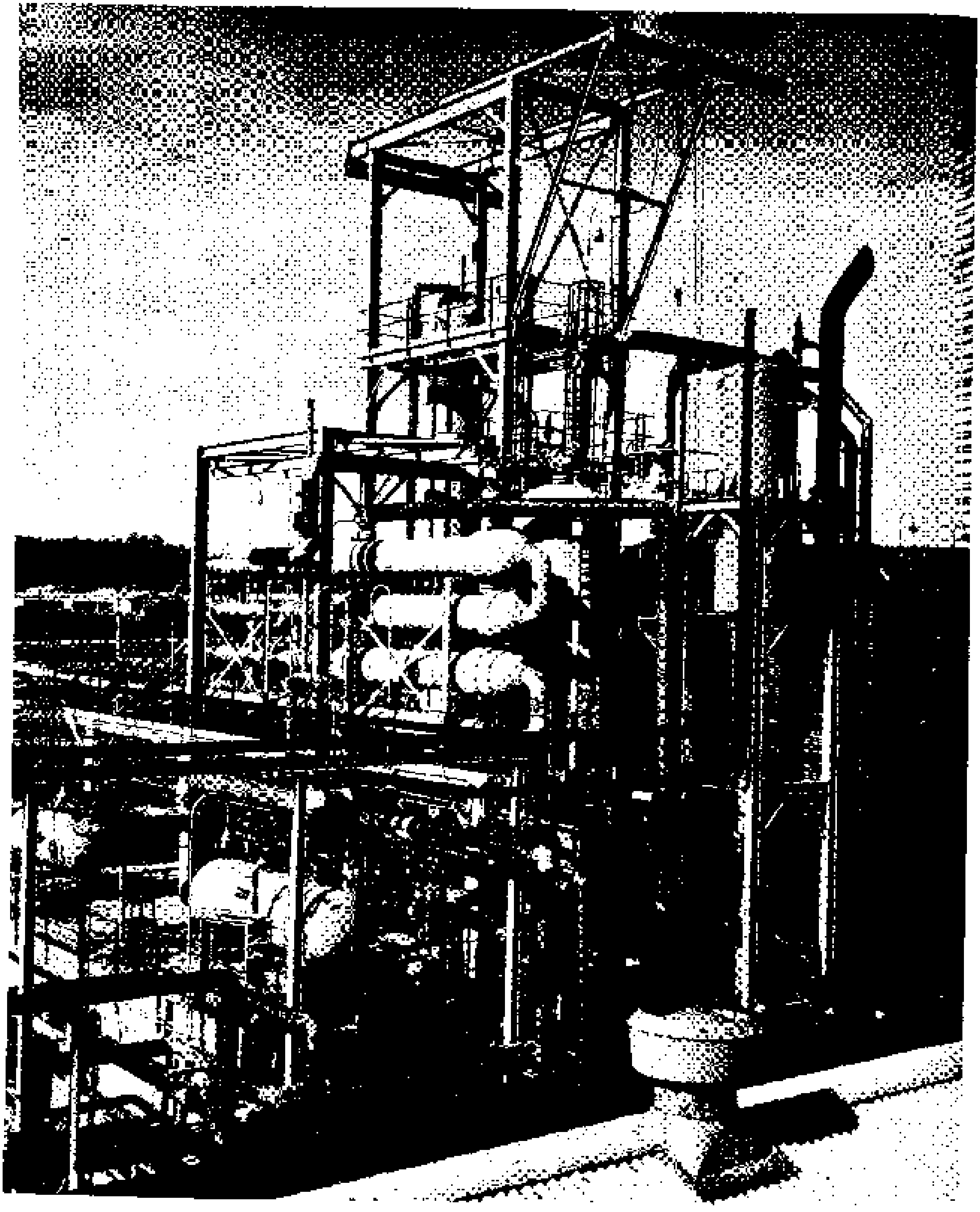

Figure 20. - Synthesis structure showing heat-exchange equipment (light vessels) and Fischer-Tropsch reactor (dark vessel at right center).

velocity limits, it became necessary to modify the synthesis reactor. This modification consisted of installation in the reactor of a steel liner backed up by a ceramic mass, reducing the reactor diameter from 6 feet to 3.

Choice of a ceramic material for backing up the steel liner required considerable study and experimentation before a material was found that was dense enough and one which would not disintegrate upon heating to reaction temperature. It was essential that this backing material be sulfur-free to protect the catalyst. It also was essential that the material be available in a puttylike form to provide a monolithic lining. The material finally employed was a sand-lime mixture that could be made up as a plastic putty and rammed in place between the steel liner and the outer shell of the reactor. This material was cured for several days to a hard, dense substance, using steam at 400° F.

Following installation and curing of the liner, it was impregnated with oil so that coolant oil would not be absorbed during the synthesis operation. In this impregnation treatment a coolant-oil fraction obtained from the distillation of East White Lake crude oil was employed. Heating to near reaction temperature completed the impregnation treatment.

With the modified reactor described above, it is possible to operate at the optimum oil velocities required to disperse the catalyst and at gas space velocities from 300 to approximately 1,000.

To test the synthesis reactor, auxiliary equipment, and instruments, a series of circulation tests was made in which water and coarse sand, and later water and unreduced catalyst, were employed in place of the coolant oil and reduced catalyst normally used in synthesis operations. Much was learned from these operations about the functioning and limitations of equipment, and the conditions for obtaining the jiggling bed in other than a laboratory- or pilot-plant-size reactor.

The first difficulty experienced was that the coolant-oil-circulation pumps lost suction at periodic intervals. This difficulty was caused by a vortex formed in a liquid-gas separator which carried gas along with the liquid to the pump suction. This was corrected by placing a baffle in the separator in a suitable location, so that the vortex was broken. Another difficulty was that uniform distribution of gas within the jiggling bed was not obtained. This caused the gas to flow upward through the reaction space in large bubbles, creating a projectilelike effect that carried the sand over into the strainers, pumps, and other equipment. First attempt at correction was to install a screen ahead of the oil-overflow pipe, which was intended to keep the sand from being carried out of the reactor by the oil stream. The location of the gas inlet was changed, and introduction of steel balls in the bottom of the reactor to insure better dispersion of gas in the form of small bubbles in the liquid medium appeared to assist. Finally, installation of a baffle in the top of the reactor, substituting for the screen, permitted improved operation. When these tests were completed, the catalyst-water slurry was removed and the reactor allowed to drain thoroughly.

In the distillation unit, many changes in the piping, equipment, and instrumentation were found necessary. These were corrected as they were found in the course of preliminary testing operations, and by the time the first synthesis run was made, all components of the distillation system were in operating condition.

A series of actual operating tests was made on the Dowtherm vaporizer, primary fractionation system, absorbers, debutanizer, stabilizer, rerun column, and the vacuum still. One phase of these tests included distillation of 18,500 gallons of a low-sulfur crude oil from the East White Lake field into gasoline, naphtha, coolant oil, and residue fractions (fig. 21). The distilled fractions came up to all expectations and indicated that the desired cuts could be obtained in later operations. This fractionation of the crude oil yielded 8,000 gallons of a coolant-oil fraction containing 0.06 percent sulfur. This coolant oil was employed in the first synthesis run.

In these test runs, it was found that a new pump was required to transfer the primary column gasoline to the debutanizer, which operated at a pressure greater than the original pumps could generate. Various mechanical difficulties with the vacuum-distillation-system pumps and the gasoline pumps of the primary fractionator were corrected also. Outside of a few minor mechanical adjustments the Dowtherm, debutanizer, stabilizer, and rerun systems performed about as had been anticipated.

The final preparations for operation of the distillation unit included filling the converters of the Perco catalytic reforming unit with Cyclocel bauxite catalyst, and the converter of the U.O.P. catalytic polymerization unit with phosphoric acid catalyst. Following these operations, the entire distillation system was placed in standby condition ready for operation when the first synthesis run was made.

The carbon dioxide removal unit, which is used on the recycle-gas stream to the synthesis reactor and the feed-gas stream to the absorbers, required completion of its installation. The bubble-cap plates had to be installed in the reactivator, and the Raschig ring packing had to be placed in the carbon dioxide absorber. After the unit was placed in operating condition, it was subjected to various tests with water and inert gas to determine its operability. Finally, the water was drained from the system and replaced by a monoethanolamine solution, and the unit was ready for synthesis operations.

Synthesis Run 1

Synthesis run 1 had three objectives. The first was to operate the synthesis unit and obtain as great a conversion of gas into synthesis products as possible; second, to train further all operators and supervisors under actual operating conditions; and third, to observe the functioning of all equipment and instruments at operating temperatures and pressures. All three objectives were realized, and the run was considered satisfactory.

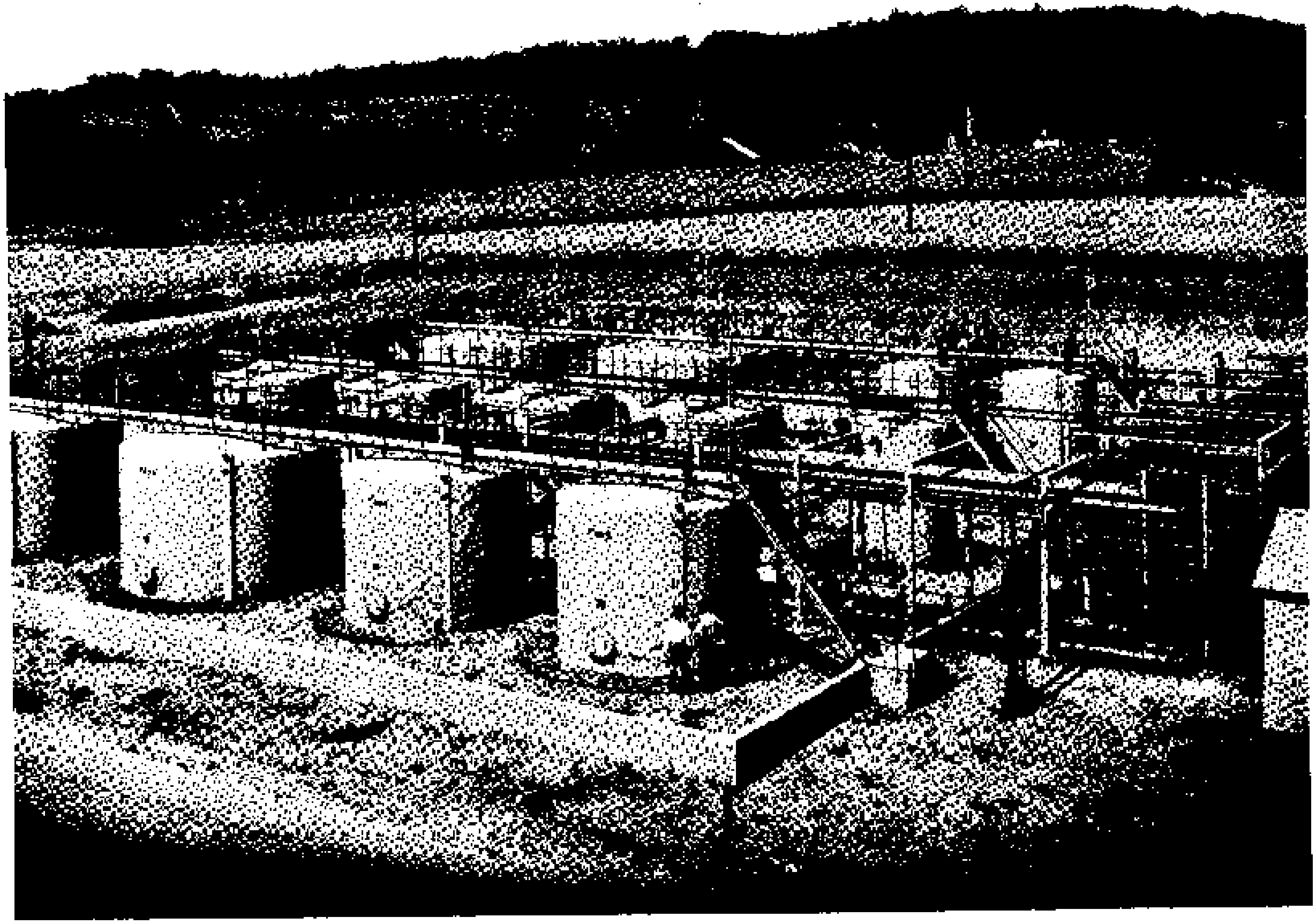

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Figure 21. - Tankage area for intermediate and finished product storage in Gas-Synthesis Plant.

The run was begun on September 4 when heating of the coolant oil and circulation of gas and coolant oil through the synthesis reactor and auxiliaries were started. The initial oil rate was 250 g.p.m. and the fresh gas-feed rate was 60,000 standard cubic feet per hour. A recycle gas rate of 60,000 standard cubic feet per hour was maintained during the early stages of the run but was abandoned when coolant-oil losses through entrainment in the gas stream became excessive. The operating pressure was maintained at approximately 325 to 330 pounds per square inch gage (p.s.i.g.) throughout the run. Enough catalyst was employed in the synthesis reactor to permit a space velocity based on anticipated fresh feed gas of approximately 600 volumes per volume per hour.

During the induction period the temperature was gradually brought up to 450° F. and then further raised by 25° F. steps until evidence of reaction was obtained. The first indications of reaction (carbon dioxide in the gas stream leaving the reactor) were obtained at 500° F. However, it was necessary to raise the temperature to 550° F. when conversion in the range of 30 to 32 percent was obtained. The operating conditions existing during the latter part of the run were as follows:

Synthesis run 1

Average conditions for period of September 9-12, 1951

Maximum temperature, top of reactor	°F.	549
Temperature difference across reactor	do.	9
Maximum reactor pressure	p.s.i.g.	330
Pressure differential across reactor	do.	22
Fresh feed gas flow rate	std. cu. ft. hr.	56,300
Recycle ratio		No recycle
H_2:CO ratio, fresh gas feed		0.82
H_2 + CO conversion	percent	31
Usage ratio, H_2:CO		0.68
CO_2 in fresh gas feed	percent	1.6
CO_2 in gas stream leaving reactor	do.	11.8
CO_2 in tail gas stream to absorber	do.	0.1
Synthesis products	gm./cu. m. H_2 + CO feed (theo.)	64.5

The run was terminated on September 12 after 8 days of operation. It was evident that the catalyst activity was low, and this can be attributed to the following factors:

(1) The catalyst employed in this run was the first to pass through the reduction equipment and was not uniformly reduced. The percentage of reduction varied between zero and 100 percent and probably averaged about 70 percent.

(2) The catalyst was stored under coolant oil which contained 0.06 percent sulfur. Although the amount of sulfur was low, it could have had a deleterious effect on the catalyst.

(3) The circulating coolant oil in the system initially contained 0.06 percent sulfur, but this was reduced as the reaction progressed.

(4) The synthesis fresh feed gas contained excessive amounts of sulfur during the early stages of the synthesis.

Some of the difficulties experienced during this first synthesis run were corrected after the run was terminated, and the units were prepared for the second synthesis run which was made during October and November.

Synthesis Run 2

The synthesis and distillation units were operated in conjunction with the Kerpely gasifier and purification unit in a second synthesis run from October 23 to November 18, 1951. Included were the Fischer-Tropsch reactor system, the primary distillation column, the light-ends absorbers and stripper, the polymerization reactor, and the final stabilizer and rerun columns. Operation of the various units was relatively smooth, but some improvements in instrumentation and control could have added measurably to ease of operation.

Fourteen thousand pounds of reduced synthetic ammonia-type conversion catalyst, prepared and reduced in the plant, was charged to the synthesis converter on October 21 and 22, 1951. The catalyst was estimated to be approximately 90 percent reduced. This weight of catalyst had a volume of approximately 116 cubic feet, and permitted a space velocity of 550 volumes per volume per hour with a fresh synthesis gas feed rate of 65,000 standard cubic feet per hour. The reduced catalyst had been covered with a sulfur-free oil to prevent deterioration of the catalyst after reduction and during the storage period of approximately 6 months. Additional coolant oil, the fraction of East White Lake crude that had been used in the first synthesis run, was charged to the synthesis converter on October 23, 1951. After raising the pressure in the synthesis unit to 330 p.s.i.g., circulation and heating of the coolant oil to reaction temperature and the flow of synthesis gas to the converter were started. The initial oil circulation rate was 250 g.p.m., and the initial fresh synthesis-gas feed rate was approximately 62,000 standard cubic feet per hour. No recycle-gas flow was employed at the start.

A stepwise induction procedure was employed. This was similar to the procedure employed at the Bruceton laboratories but differed in the temperature and conversion levels used. This operation covered 5 days. The following shows the temperatures and conversions obtained during the catalyst induction period:

Catalyst induction

Date	Fresh feed rate, std. cu. ft. hr.	Recycle-feed rate	Temperatures, °F.		Conversion, percent
			In reactor	Out reactor	
10-23-51	61,600	None	294	294	-
10-24-51	63,200	1.13	428	431	13.5
10-25-51	61,500	1.27	451	457	21.5
10-26-51	63,100	1.27	474	485	35.6
10-27-51	64,700	1.27	505	522	62.0
10-28-51	63,900	1.36	509	524	71.6

Pressures were maintained within the range of 327 to 334 p.s.i.g. and oil circulation rates from 300 g.p.m. at the start to 500 g.p.m. during the latter phases of the induction period and during the synthesis period.

After the induction was completed, the temperatures during synthesis operations were maintained between 522° to 528° F., and conversions ranging from 71.6 to 85.9 percent were obtained. Conversion relates to the percentage of hydrogen and carbon monoxide consumed in the reaction, as determined by analysis of the inlet and outlet gas streams and volumes of each. No attempt was made to obtain maximum conversion, as the objectives of this run were to test the equipment and process for operability over an extended time.

Table 10 shows actual operating data obtained during a 5-day period of the run. The results are not intended to represent the optimum conditions or yields, which are to be determined in future runs.

These operations were conducted on a continuous basis from the start until the run terminated at the end of 25 days, with one exception. A forced shut-down, occurring on November 11 and lasting for 30 hours, owing to an interruption of the 275-p.s.i.g. steam supply to the entire synthesis area, was successfully bridged and gave the operators valuable experience in handling an unexpected situation. Although some drop in catalyst activity resulted from this interruption, 75-percent conversions were still obtained at 525° F. at the termination of the run. The final shut-down was routine.

Distillation of the synthesis condensate into gasoline, Diesel oil, cracking-stock, and coolant-oil fractions was accomplished during the latter part of November. The principal products, gasoline and Diesel oil, will be upgraded by further treatments and will be available in barrel quantities for evaluation and testing.

TABLE 10. - Average operating conditions, synthesis run 2

Date	11-2-51	11-3-51	11-4-51	11-5-51	11-6-51
Fresh feed gas flow .... std. cu. ft. hr.	62,700	62,200	62,600	63,200	61,900
H_2:CO fresh feed gas	0.76	0.80	0.80	0.79	0.76
Recycle ratio	1.45	1.58	1.55	1.53	1.63
Maximum temperature .... °F.	523	522	523	522	524
dT across converter .... do.	15	14	15	14	15
Maximum pressure .... p.s.i.g.	327	330	329	330	329
dP across converter .... p.s.i.	30	30	31	31	30
Space velocity .... vol./vol./hr.	538	534	537	542	531
Conversion .... percent	81.9	81.7	80.6	79.8	85.9
Usage ratio	0.70	0.71	0.70	0.71	0.71
CO_2:					
In fresh feed gas .... percent	1.5	2.2	1.6	2.5	2.0
In recycle gas .... do.	1.9	0.0	0.1	0.4	0.1
In gas from synthesis converter .... do.	12.5	11.8	11.5	11.4	12.2
$C_1 + C_2$ yield .... gm./m^3 ($CO + H_2$) in fresh feed	35.7	35.6	34.2	29.0	24.6
C_3 + yield ..... gm./m^3 ($CO + H_2$) in fresh feed (theo.)	134.6	135.3	133.5	137.0	154.0