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USE OF A LARGE-DIAMETER
REACTOR IN SYNTHESIZING
PIPELINE GAS AND GASOLINE
BY THE HOT-GAS-RECYCLE PROCESS

By A. J. Forney, D. Bienstock, and R. J. Demski



UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

1962

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* * * * * report of investigations 6126



UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

BUREAU OF MINES
Marling J. Ankeny, Director

The work upon which this report is based was done partly under a cooperative agreement between the Bureau of Mines, U.S. Department of the Interior, and the Consolidated Natural Gas Company, Pittsburgh, Pa.

This publication has been cataloged as follows :

Forney, Albert J

Use of a large-diameter reactor in synthesizing pipeline gas and gasoline by the hot-gas-recycle process, by A. J. Forney, D. Bienstock, and R. J. Demski. [Washington] U. S. Dept. of the Interior, Bureau of Mines [1962]

ii, 30 p. illus., tables. 27 cm. (U. S. Bureau of Mines. Report of investigations, 6126)

Based on work done in cooperation with the Consolidated Natural Gas Company, Pittsburgh, Pa.

I. Gas, Natural. 2. Gasoline. I. Title. II. Title: Reactor in synthesizing pipeline gas. III. Title: Hot-gas-recycle process. (Series)

TN23.U7 no. 6126 622.06173

U. S. Dept. of the Int. Library

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USE OF A LARGE-DIAMETER REACTOR IN SYNTHESIZING PIPELINE GAS AND GASOLINE BY THE HOT-GAS-RECYCLE PROCESS

by

A. J. Forney,¹ D. Bienstock,¹ and R. J. Demski²

ABSTRACT

The hot-gas-recycle process, for the hydrogenation of carbon monoxide, was investigated in a 12-inch-diameter reactor. Initially because the distribution of gas was poor, hotspots developed in the catalyst bed. After the velocity profile of the gas flowing through the bed was studied, the method of packing the catalyst was altered. Because this change improved the distribution of gas, temperature control was excellent.

The 12-inch-diameter reactor was operated successfully in the synthesis of gaseous and liquid fuels. When high-Btu gas was synthesized in two stages, parallel-plate assemblies of Raney nickel were almost as active as granular Raney nickel in the second reactor. The pressure drop through the second reactor, however, was reduced 90 percent by the use of these assemblies.

INTRODUCTION

Although the 1960 proved reserves of natural gas in the United States are considered sufficient for the next 20 years,³ the price of natural gas is expected to increase. Because of this increase, a synthetic pipeline gas from coal may become competitive with the natural product before the reserves are depleted. The Bureau of Mines is conducting an engineering investigation of the synthesis of liquid and gaseous fuels from coal by first gasifying the coal to give hydrogen and carbon monoxide, and then reacting these gases over catalysts. One of the more promising techniques for conducting this reaction is the hot-gas-recycle process, in which the exothermic heat of reaction (about 70 Btu per cubic foot of $H_2 + CO$ converted) is removed from the catalyst by circulating large volumes of recycle gas. The Bureau has improved the

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³ Industrial and Engineering Chemistry. Symposium on High-Btu Gas. Vol. 52, 1960, pp. 575-598.
Chemical Week. Energy Outlook, A Chemical Week Report. May 14, 1960, pp. 64-89.

hot-gas-recycle process by using steel lathe turnings as the catalyst. This high void catalyst offered lower resistance to gas flow while still maintaining excellent temperature control and catalyst activity. For example, 20 volumes of recycle gas for each volume of synthesis gas has been found satisfactory, permitting a temperature rise of 40° to 50° C through a 10-foot bed of a 3-inch diameter reactor.⁴ Use of a granular catalyst required 100 volumes of recycle gas for temperature control in early German experiments.⁵ This large flow through a granular catalyst would result in a pressure differential more than 100 times as great as that obtained with lathe turnings.

Heat transfer was poor in the German work in a hot-gas-recycle system of large size. It was deemed advisable to study the operability of our system with a catalyst of lathe turnings in a reactor of greater cross section than the 3-inch diameter vessel. A reactor 12 inches in diameter was installed with strategically located thermocouples to closely measure temperature gradients and heat transfer characteristics. This report describes the operation and the results.

EXPERIMENTAL PROCEDURE

Method of Operation and Description of Apparatus

Synthesis

Figure 1 shows a flowsheet of the pilot plant for the synthesis of gaseous fuels. Two reactors are used in series: The first employing a steel catalyst converts 70 to 80 percent of the synthesis gas; the second using Raney nickel converts the remainder. The total feed gas flows down through the main reactor, passes through the cyclone trap, and then is divided. If the second reactor is not in service, the part of the stream that has been cooled, depressurized, and metered, leaves the system as product. The remainder is recompressed and recycled to the reactor, 5 to 10 percent as cold gas and the rest as hot gas. The ratio of cold to hot gas is used to control the water vapor content of the total recycle gas returning to the reactor. The synthesis gas, dried and desulfurized by flowing through silica gel and activated carbon, combines with the cold and hot recycle streams and flows to the main reactor.

The main reactor is a 12-inch-diameter pipe containing 2 cubic feet of catalyst in a 3-foot bed. Figure 2 is a photograph of and figure 3 is a sketch of the reactor and thermocouple distribution. There were 41 thermocouples arranged in 7 levels spaced 6 inches apart. They were 1 inch from the

⁴Bienstock, D., J. H. Field, A. J. Forney, and R. J. Demski. Pilot Plant Development of the Hot-Gas-Recycle Process for the Synthesis of High-Btu Gas. BuMines Rept. of Inv. 5841, 1961, 27 pp.

Field, J. H., D. Bienstock, A. J. Forney, and R. J. Demski. Further Studies of the Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Hot-Gas-Recycle Process). BuMines Rept. of Inv. 5871, 1961, 32 pp.

⁵Storch, H. H., N. Golumbic, and R. B. Anderson. The Fischer-Tropsch and Related Syntheses. John Wiley and Sons, Inc., New York, N.Y., 1951, 610 pp.

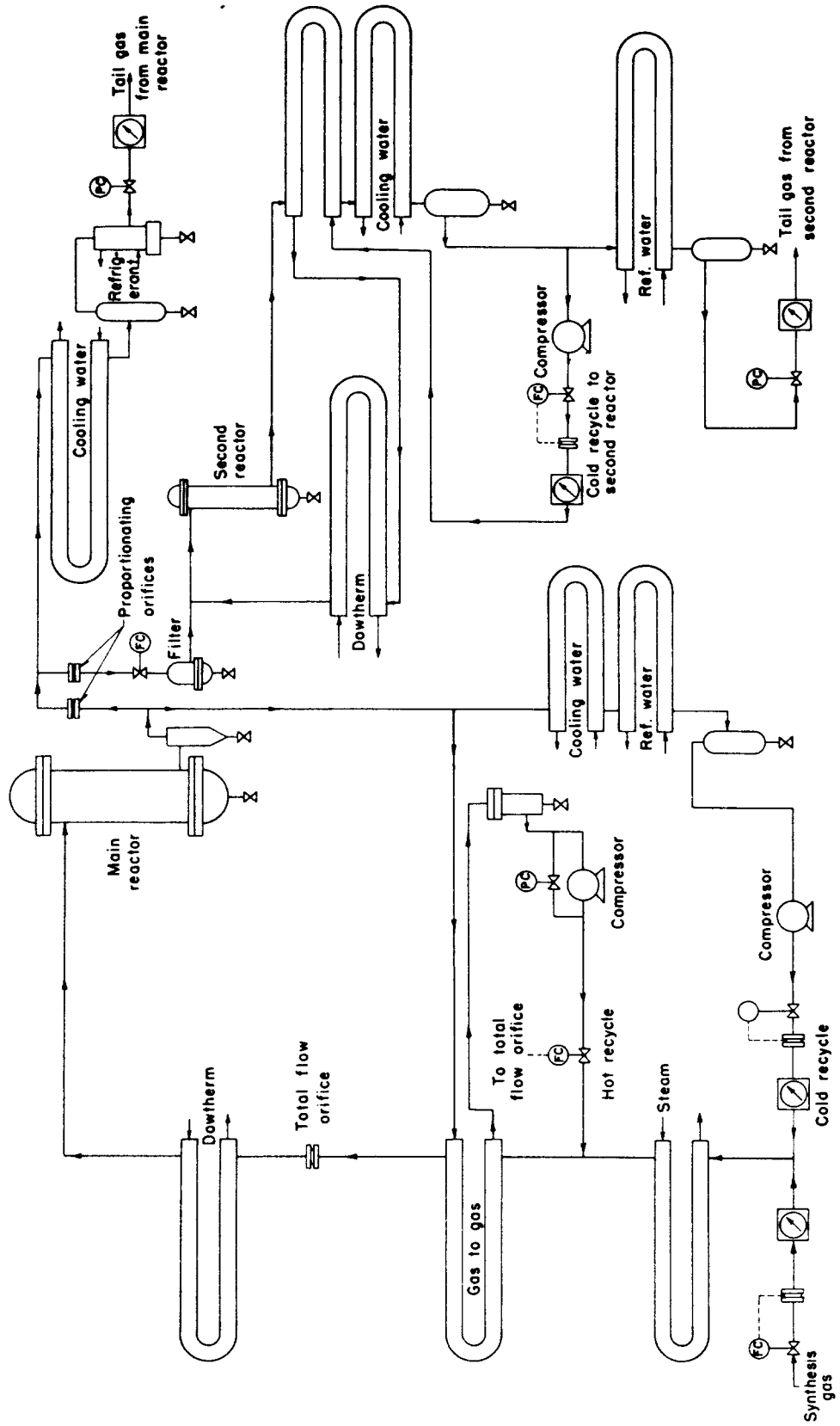


FIGURE 1. - Schematic Flowsheet of Hot-Gas-Recycle Process for High-Btu Gas Production.

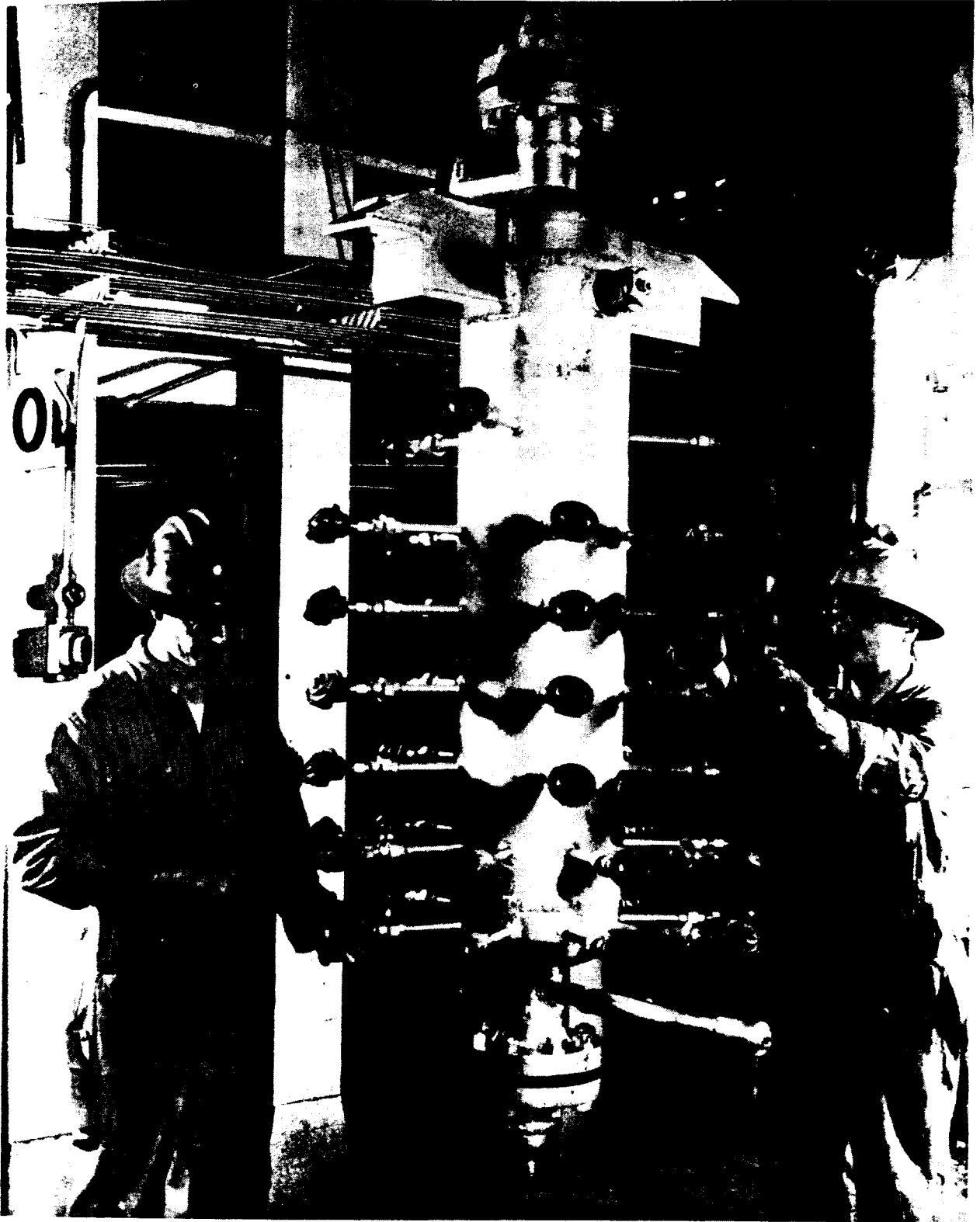


FIGURE 2. - The 12-Inch-Diameter Main Reactor for the Hot-Gas-Recycle Pilot Plant.

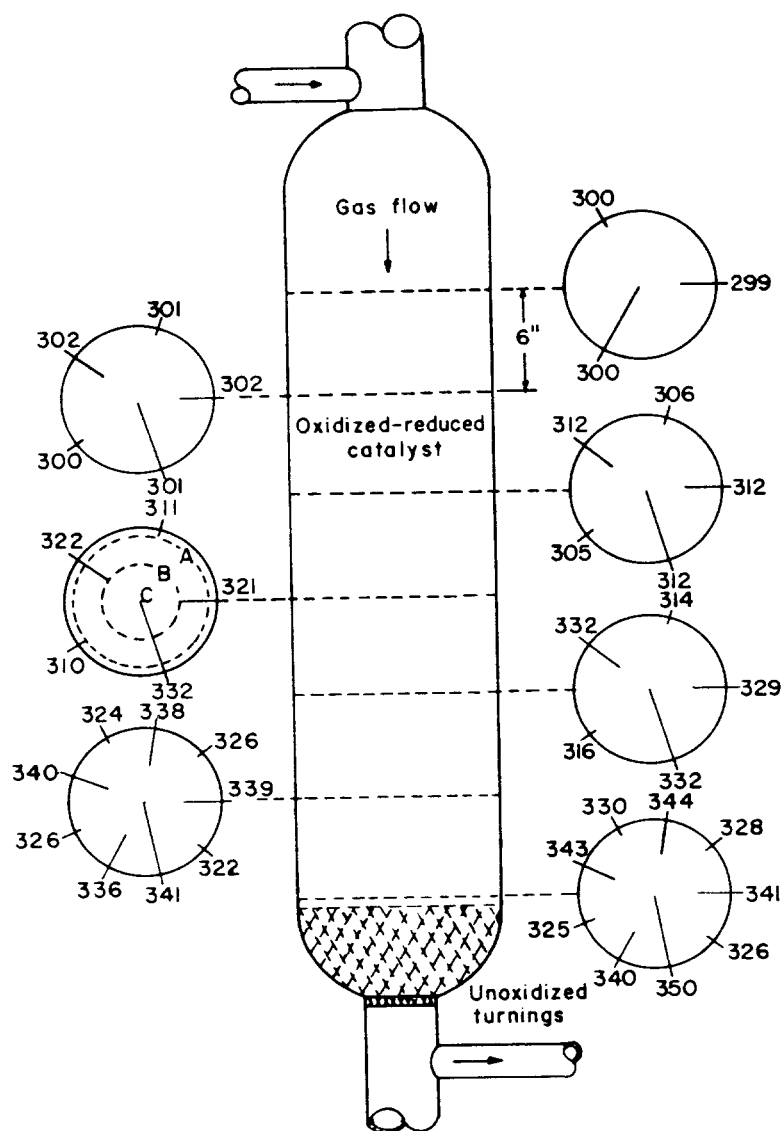


FIGURE 3. - Location and Temperature of Thermocouples in the 12-Inch Reactor in Experiment 22. A, 1 inch from wall; B, 3/2 inches from wall; C, center of bed; temperatures, °C.

wall, 3-1/2 inches from the wall, and at the center. Above the catalyst, three thermocouples were placed on one level; in the bed five thermocouples were arranged on each of four levels; nine thermocouples were set on each of the two bottom levels. (Temperatures shown in figure 3 are those obtained in experiment 22 discussed later.)

When the second reactor is in service, the tail gas from the main reactor is not cooled but flows into the second reactor. From the second reactor the effluent gas is cooled (lack of a hot gas compressor for the second reactor system makes this cooling necessary in these experiments). Part of the cooled stream is depressurized, metered, and analyzed as the product gas; the remainder is recompressed, reheated, and recycled to the second reactor.

The second reactor is a 3-inch, schedule 80 pipe, 3-1/2 feet long. The effluent gas from the first reactor passes through a porous plate filter (fig. 1) to prevent carbon or fines from being carried into the second reactor from the first.

Hot Gas Compressor

The hot gas compressor is shown in a photograph, figure 4. It is a single-cylinder, double-acting, reciprocating compressor. The gas is compressed from 400 to a maximum of 500 psig, and can be operated at temperatures as high as 325° C. The capacity at these conditions is 27,000 standard cubic feet per hour at a flywheel speed of 300 revolutions per minute. Changing the speed of the flywheel to 400 revolutions per minute increased the capacity to 36,000 standard cubic feet per hour.

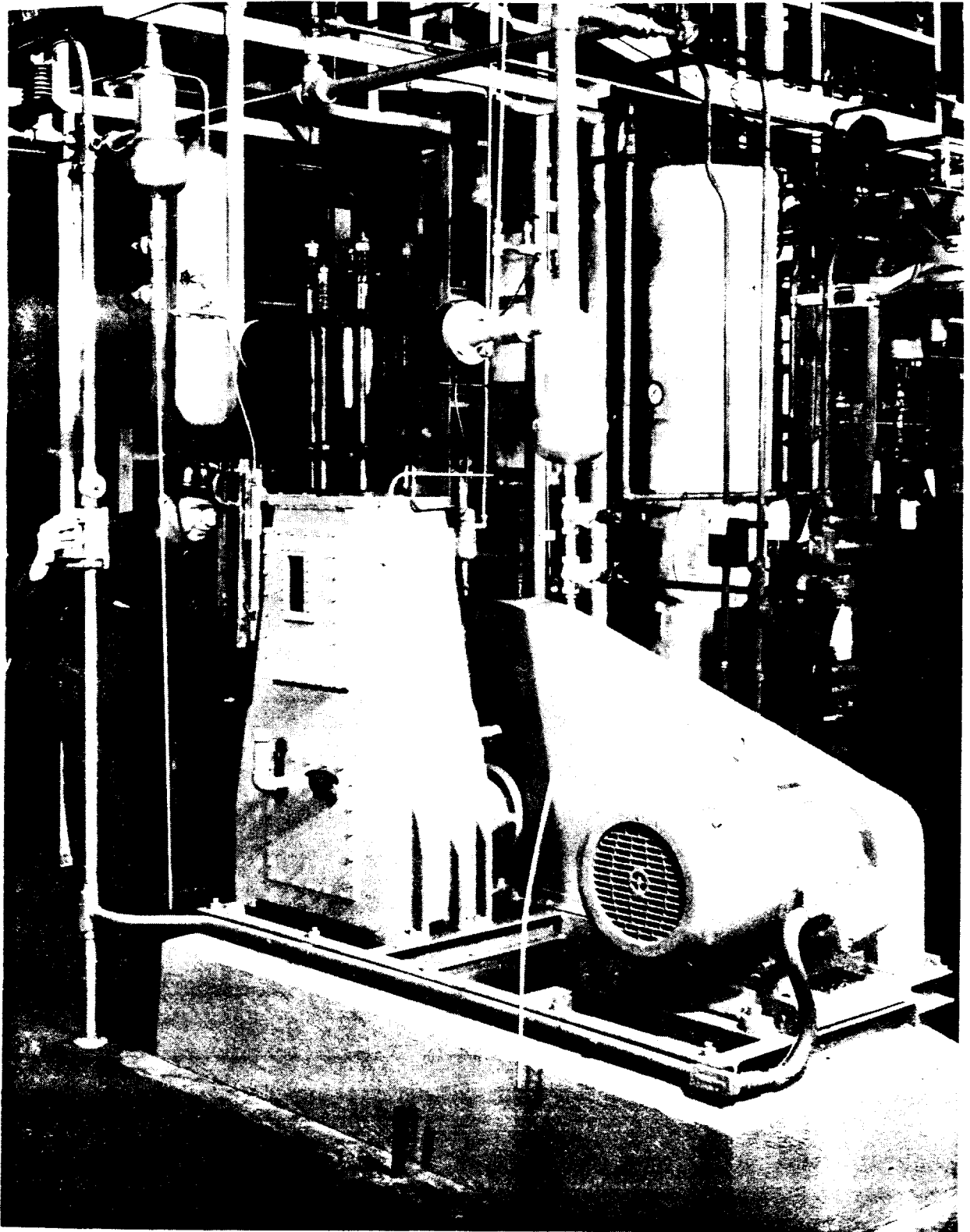


FIGURE 4. - Hot-Gas-Recycle Compressor.

Because the catalyst must not be subjected to sulfur compounds present in most petroleum-derived oils and because the compressor must be operated at high temperatures, a special lubricant made from polyalkylene glycols was used. This sulfur-free lubricant is noncarbonizing, non-gum-forming, and noncorrosive to the compressor.

Preparation of Catalysts

Steel Turnings

The steel turnings used as catalyst in the main reactor were machined from 1018 carbon steel. The cutting depth, angle, and speed of the lathe was adjusted to produce turnings with void volumes of 84 to 87 percent.⁶ These turnings were oxidized with steam at atmospheric pressure and 600° C until 20 percent of the iron was converted to Fe_3O_4 ($3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$). A steam flow of 400 volumes an hour per volume of turnings was used. The surface of the turnings was oxidized to magnetite, whereas the core was unaffected.

The oxidizer shown in figure 5 is a 6-inch pipe made of 304 stainless steel. It has a capacity of 0.3 cubic foot. As the synthesis reactor

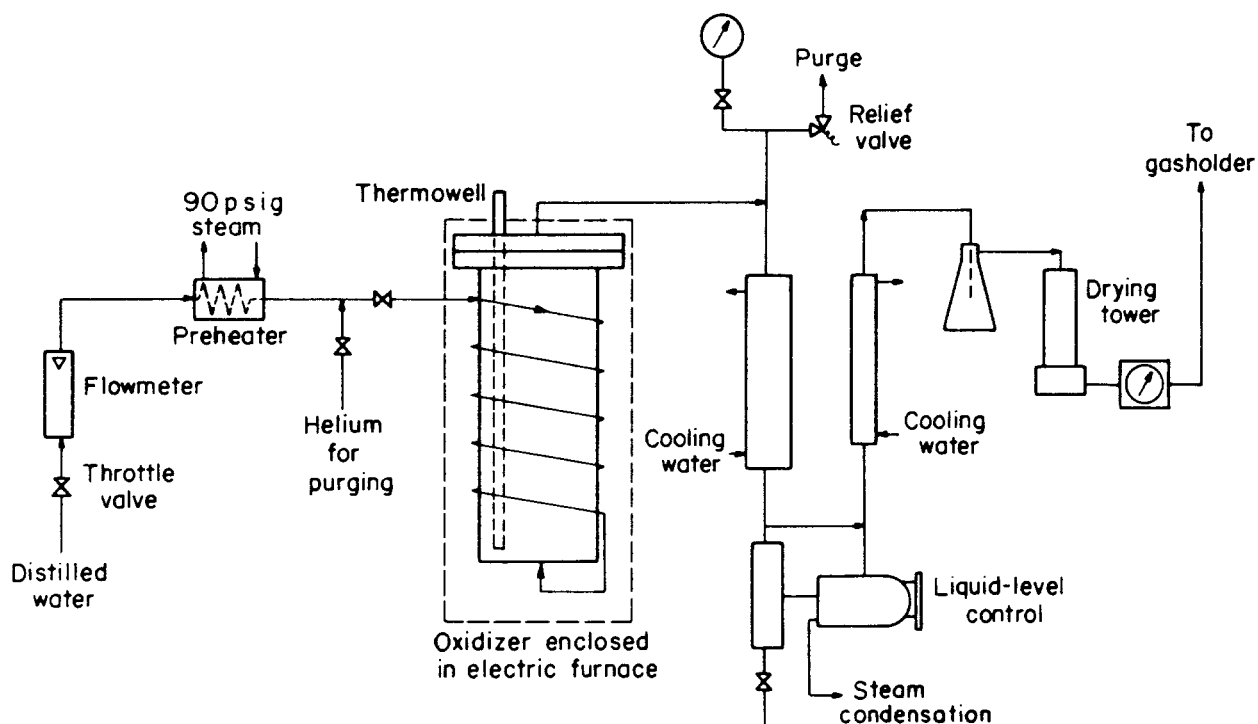


FIGURE 5. - Oxidation Unit for Preparing the Steel Catalyst for the Hot-Gas-Recycle Process.

⁶ Bienstock, D., R. M. Jameson, J. H. Field, and H. E. Benson. The Fischer-Tropsch Synthesis Using Gas Recycle Cooling (Simulated Hot-Gas-Recycle Process). BuMines Rept. of Inv. 5655, 1960, 25 pp.



FIGURE 6. - Parallel Plate Assembly of Raney Nickel Catalyst.

and dried at 200° C at a vacuum of 2 millimeters of mercury. The fines were removed, and only particles between 4- and 20-mesh were used. This treatment produces a finely divided, active surface of nickel.

Two Raney nickel plate assemblies were used during the latter part of experiment 25. These assemblies, each 3 inches in diameter by 6 inches high, were machined from an ingot of Raney nickel. Figure 6 shows a photograph of an assembly. The spacers, rods, and rivets that hold the sections together were made of commercial nickel. These assemblies were activated by immersion in a 5-percent sodium hydroxide solution for 3 hours to remove part of the aluminum. After the assemblies had been installed in the reactor, they were dried with flowing hydrogen overnight in the reactor at 200° to 300° C.

contains 2 cubic feet of catalyst, seven charges of the oxidizer were needed. Steam used for oxidation is prepared from distilled water. This method eliminates the noncondensable gases, which are present in small amounts in the steam utility lines in the plant. The unreacted steam is condensed, and the evolved hydrogen is dried and metered. The yield of hydrogen indicates the degree of oxidation.

In experiment 26 for the production of liquid hydrocarbons, the oxidized turnings were alkalinized by impregnating with K_2CO_3 . The turnings were immersed in a 6-percent solution of K_2CO_3 for 10 minutes, then dried with air, and finally dried further in an oven overnight. For the synthesis of gaseous hydrocarbons, the oxidized turnings were not alkalinized.

The oxidized turnings were reduced with hydrogen in the 12-inch-diameter reactor at 400° C in all experiments, using a cold recycle-to-fresh feed ratio between 40 and 80. The period of reduction was 60 hours, except for 90 hours in experiment 26.

Raney Nickel

Raney nickel, an alloy of 58 percent aluminum and 42 percent nickel (Al_3Ni), was the catalyst for the second reactor. To activate the nickel, the alloy was leached with a 25-percent aqueous solution of sodium hydroxide for 3 hours to remove part of the aluminum, washed with water,

Table 1 summarizes catalyst information in experiments 22 through 26.

TABLE 1. - Summary of catalyst data for experiments 22 through 26

Experiment	Catalyst, main reactor						
	Steel lathe, turnings, type	Voids, percent	Oxidation, percent	Charge		K ₂ O content, percent	On stream, hours
				Pounds	Volume, cu ft		
22.....	1018	87	20	129.3	2	0	1,020
23.....	1018	86	20	134.4	2	0	718
24.....	1018	84	20	158.0	2	0	1,003
25.....	1018	84	20	152.5	2	0	1,177
26.....	1018	84	20	151.1	2	.17	1,102

	Catalyst, second reactor				
	Type	Mesh size	Charge		On stream, hours
			Pounds	Volume, cu ft	
22.....	Raney nickel	4-20	1.73	0.016	500
23.....	do.	4-20	4.29	.046	235
24.....	do.	4-20	4.29	.046	¹ 1,008
25.....	do.	4-20	4.29	.046	² 1,248
25.....	do.	(³)	4.92	.046	480
26.....	(⁴)	(⁴)	(⁴)	(⁴)	(⁴)

¹ Includes experiments 23 and 24.

² Includes experiments 23, 24, and 25.

³ Plate assemblies.

⁴ Not in service.

Synthesis of High-Btu Gas

Operation With Single Reactor

Experiments 22, 23, 24, and 25 were performed in the hot-gas-recycle pilot plant for the synthesis of high-Btu gas.

During experiment 22, the 12-inch reactor operated satisfactorily for the first 400 hours at a feed-gas rate of 1,700 standard cubic feet per hour (850 volumes of gas per hour per volume of catalyst) with a feed gas of 3H₂+1CO composition. Because the bed of catalyst was shallow, the superficial linear velocity was only 1.1 feet per second at a recycle ratio of 22:1 (37,400 standard cubic feet of recycle gas per hour to 1,700 standard cubic feet of feed gas per hour). This velocity may be compared with a linear velocity of 3.6 feet per second in the 3-inch-diameter reactor. The maximum temperature at the bottom of the reactor was 350° C; inlet temperature was 300° C; other temperatures are shown in figure 3. As expected, the temperature gradually rose in the reactor in the direction of flow from top to bottom as the heat of reaction was absorbed by the circulating gas. The radial gradient of 25° between the center and the wall at the bottom layer was unexpected, but caused no

difficulty. Figure 7 illustrates the gradients after 272 hours of operation. When more than one thermocouple was on the same level and in the same radius, the temperature readings are averaged.

After 400 hours, the catalyst temperatures at the bottom of the bed increased. At 778 hours of synthesis (fig. 7), the maximum temperature was almost 500° C, and other temperatures in the bottom 6 inches of the bed started to increase. However, the gas outlet temperature was 335° C, an increase of only 35° C from the inlet. The runaway temperatures therefore were localized hotspots and not the average temperature of the gas stream.

Attempts to control the hot zone by changing operating conditions proved ineffective. The hot-gas-recycle flow was already at a maximum. The experiment was therefore ended because temperature control was poor.

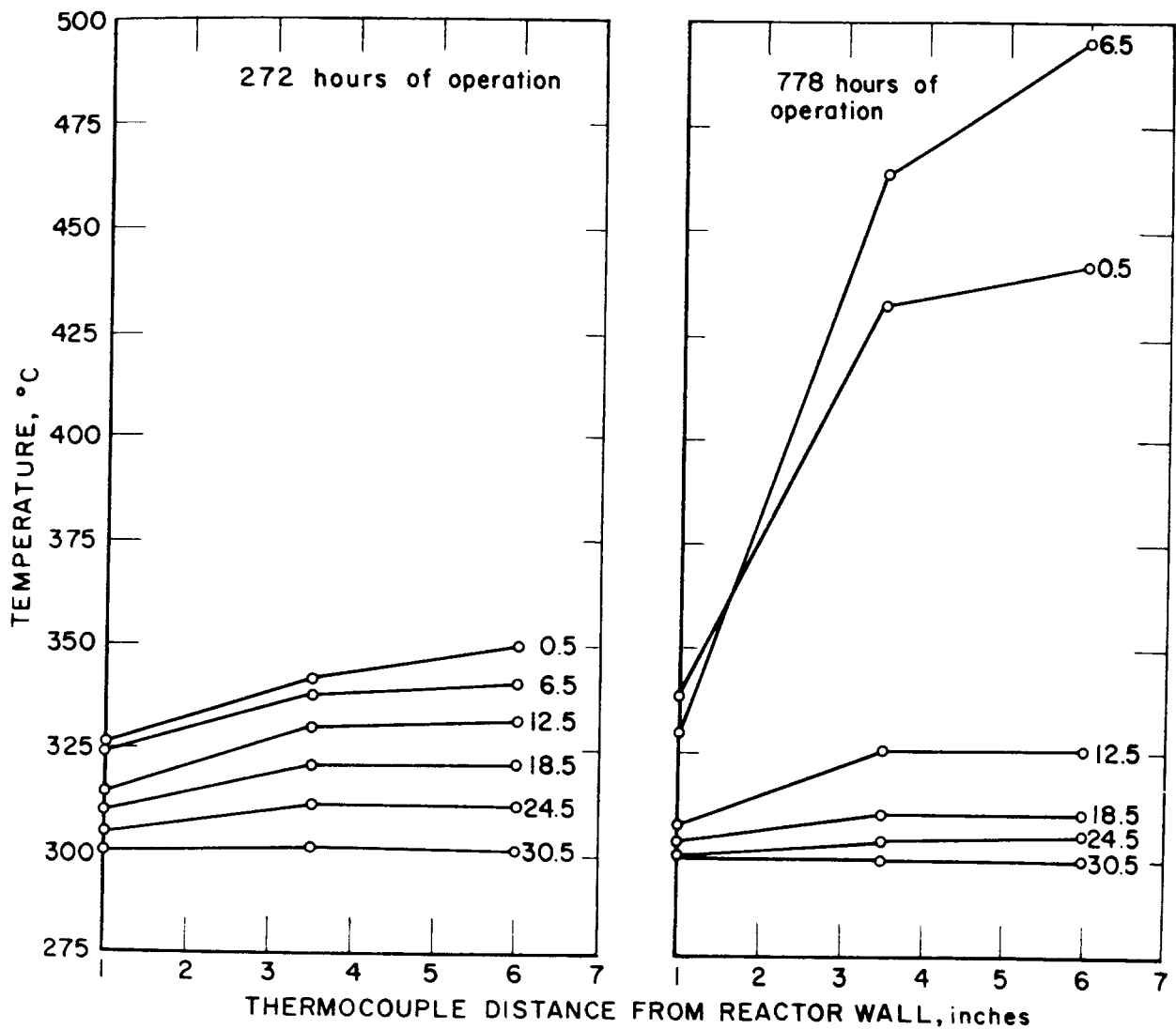


FIGURE 7. - Temperature Gradients in Catalyst Bed, Experiment 22.

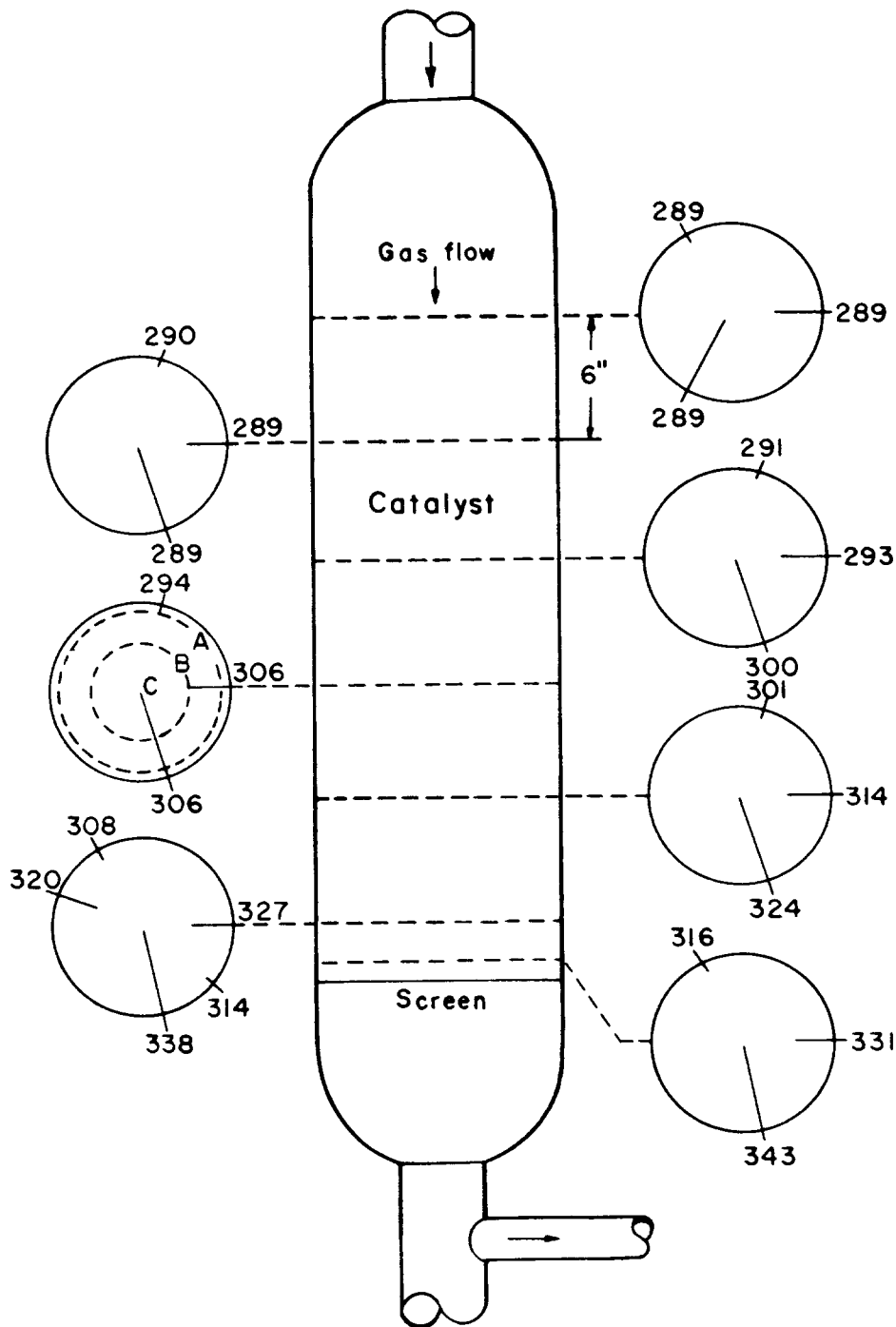


FIGURE 8. - Location and Temperature of Thermocouples in the 12-Inch Reactor in Experiment 23. A, 1 inch from wall; B, 3½ inches from wall; C, center of bed; temperature, °C.

The cause of local overheating was suspected of being uneven gas distribution and subsequent poor convective heat transfer at the low-velocity zone. Inadequate transfer of heat resulted in a hot-spot. Because the temperature at this spot was high, carbon was deposited according to the reaction, $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$. The carbon further impeded the flow of gas and the transfer of heat from the catalyst to the gas. Consequently, the hotspot gradually spread. This explanation is supported by the large quantities of carbon found in the bottom 16 inches of the bed upon removal of the catalyst.

A series of tests was made to determine gas distribution through the catalyst bed. A superficial linear velocity of 1 foot per second was used at atmospheric temperature and pressure. A commercial air

meter measured flows up to 100 feet per second on a logarithmic scale. A screen, installed 3 inches above the bottom row of thermocouples, supported

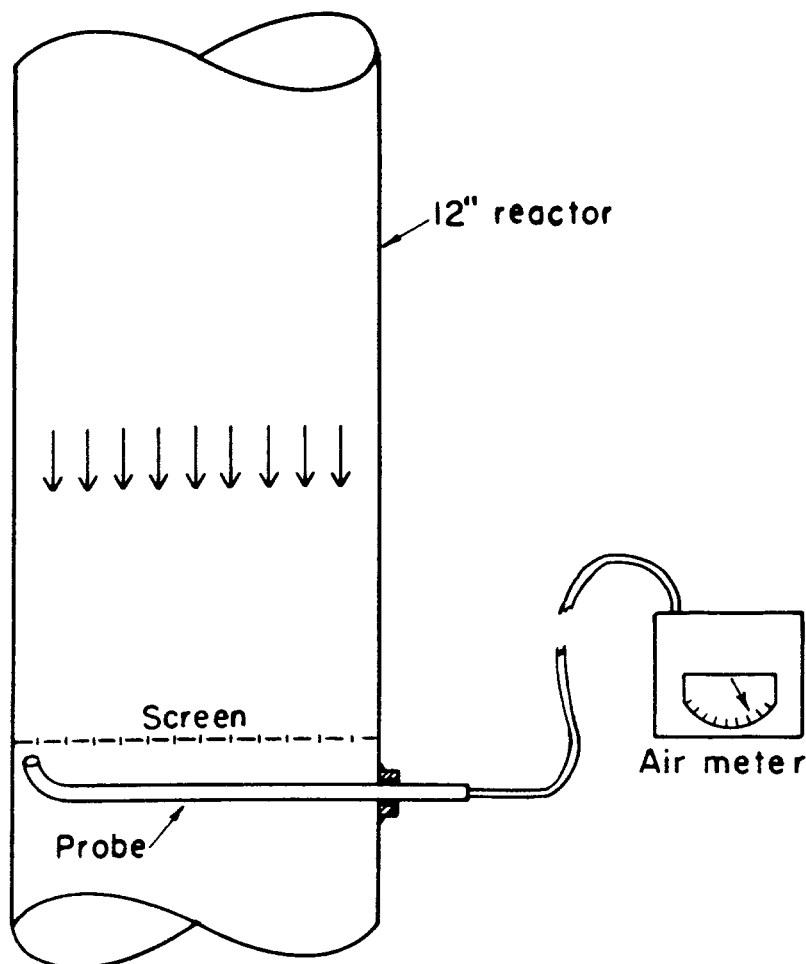


FIGURE 9. - Method of Taking Velocity Profile in the 12-Inch Reactor.

the screen was installed. In the empty reactor, the maximum velocity was obtained at the center of the pipe and the minimum at the wall. After the screen was installed, an equalization of the velocity pattern was observed. The bottom graph of the figure shows the results of two tests with lathe turnings in the reactor, one with downward flow and the other with upward flow. There is a screen below the catalyst bed but none above it. The curves are similar, having minimum velocities near the center and the wall. This type of velocity profile was also found by Morales and coworkers⁷ who used a pelleted catalyst in a 2-inch reactor.

Because the large number of thermocouples may have channeled the gas along the thermocouples to the wall, the number in the bed was decreased from 38 to 20 for experiment 23. The arrangement is shown in figure 8.

⁷Morales, M., C. W. Spinn, and J. M. Smith. Velocities and Effective Thermal Conductivities in Packed Beds. Ind. Eng. Chem., vol. 43, 1951, pp. 225-232.

the bed. These bottom thermocouples were then removed, and others were installed above the screen as shown in figure 8. Figure 9 shows the location of the probe for measuring the velocity profiles. These measurements show only the flow pattern of gas emerging from the catalyst bed.

Readings were taken radially at 1-inch intervals. When the probe was inserted as far as possible into the reactor, a reading was obtained one-fourth inch from the far wall. Because of the shape of the probe, a reading was obtained no closer than 1 inch from the near wall. Because the flows indicated on the meter were not steady but fluctuated appreciably, the readings were averaged.

The top graph of figure 10 shows the velocity profiles obtained in the reactor before and after

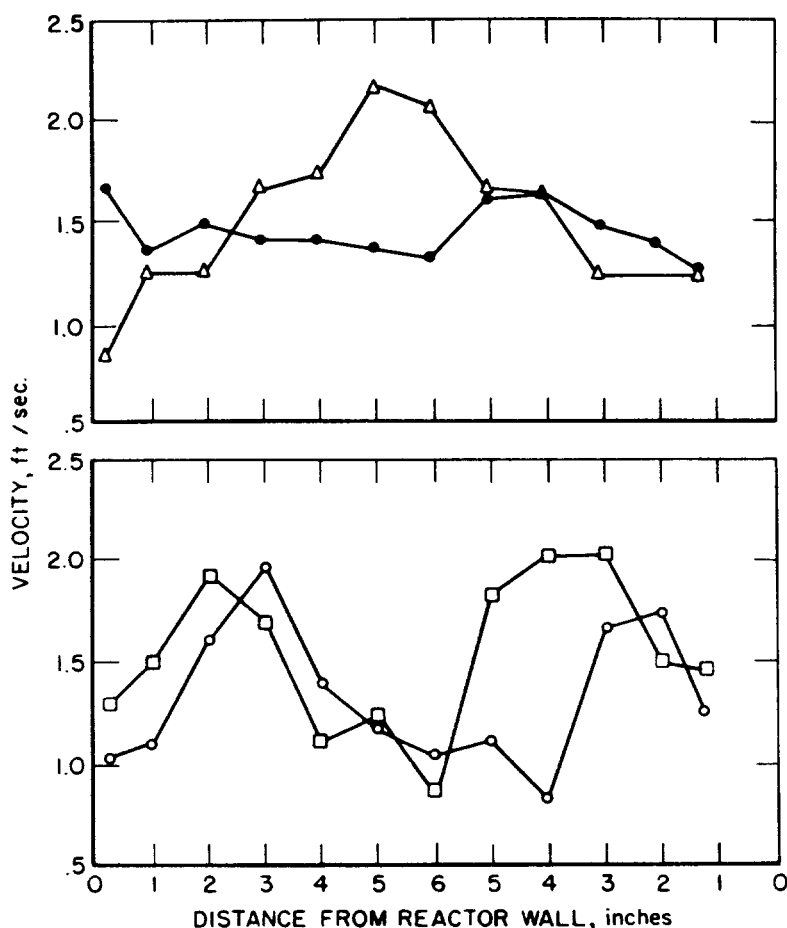


FIGURE 10. - Velocity Profiles in the 12-Inch-Diameter Reactor. Δ , gas flow down through empty reactor; \bullet , gas flow down through empty reactor and screen; \square , gas flow down through catalyst and screen; \circ , gas flow up through screen and catalyst.

packed at the wall than at the center. Figure 12 shows that the velocity profile of the catalyst of experiment 24 improved as the result of this method of charging. The gas velocity in experiment 24 was greater in the central part of the reactor--a desirable result because in previous experiments the hot zones had developed at the center.

This change in the method of packing the catalyst, maintaining the maximum temperature below 340°C , and increasing the water vapor content of the recycle gas solved the problem of controlling the bed temperatures. Figure 13 shows that the gradient from the wall to center was only 3°C at the bottom level and 8°C at the second level after 280 hours of operation, and after 780 hours of operation the gradients had actually decreased. The higher temperatures were now at the wall rather than at the center of the bed as in experiments 22 and 23. Experiment 25 verified the results of experiment 24. The

The temperature gradients taken after 260 hours of operation (figs. 8 and 11) of experiment 23 show no improvement over those obtained in experiment 22 (fig. 7), and the gradients taken after 700 hours of operation show the same uneven temperatures across the bed. The highest temperatures were at the center of the reactor and the lowest at the wall. (Only one temperature is shown at the level 0.5 inch from the bottom because the other thermocouples failed.)

In experiments 22 and 23 the catalyst had been lowered into the reactor through the 4-inch opening and distributed by spreading with a rod. In experiment 24 a new method was tried to improve the distribution of the catalyst in the bed. The catalyst was charged into the reactor through a 2-inch tube that had an inverted deflecting cone welded to the bottom. The turnings hit the outside of the cone and were diverted to the wall, so that the catalyst was more densely

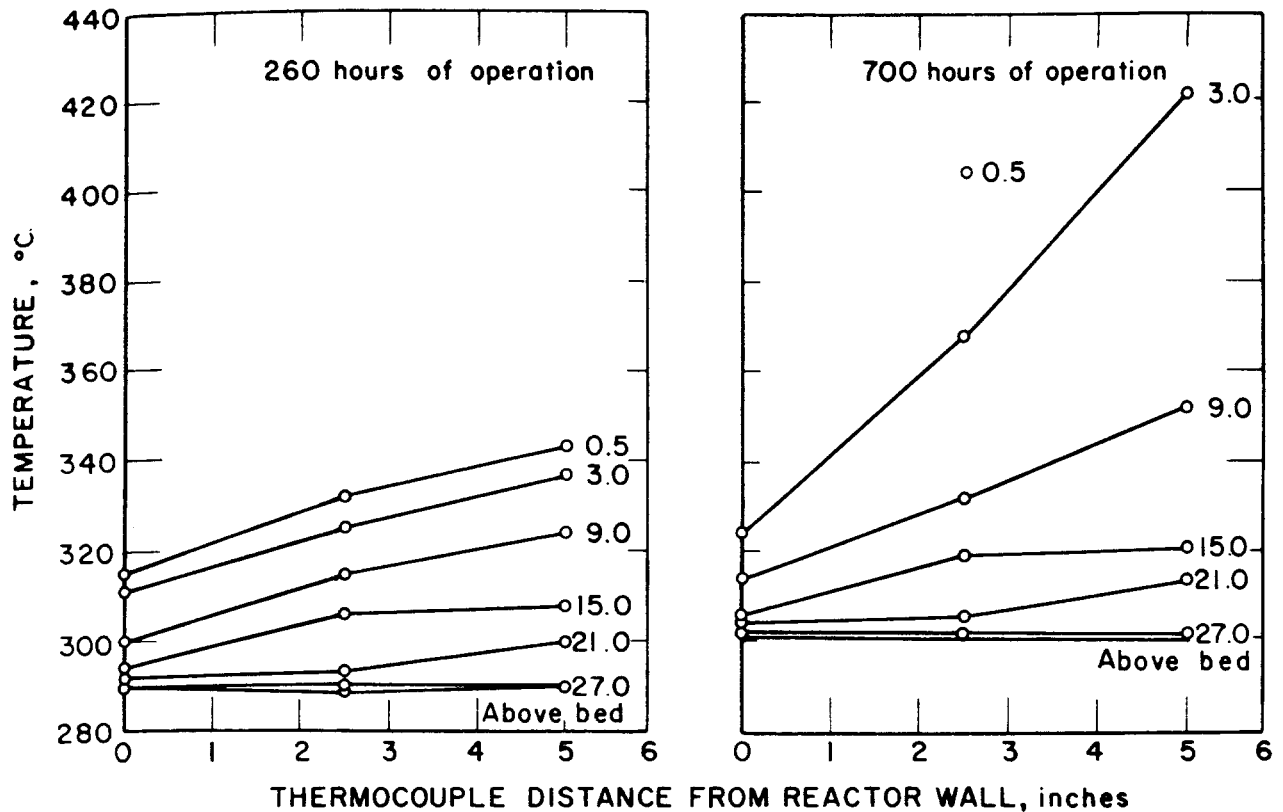


FIGURE 11. - Temperature Gradients in Catalyst Bed, Experiment 23.

large reactor was operated for over 900 hours in experiment 25 with no temperature control difficulties.

Operation With Two Reactors

Although primarily these experiments were performed to study the distribution of gas and heat in the 12-inch-diameter reactor, the second reactor containing Raney nickel was operated in experiments 22 through 25 to obtain additional data. In experiment 22, only one-fourth of the tail gas from the main reactor was used as a feed to the second reactor. In the other experiments the entire flow was used as a feed.

The temperature in the second reactor was maintained usually between 300° and 350° C by recycling 7 to 8 volumes of cold recycle for every volume of feed gas. Occasionally the temperature was increased to 400° C maximum.

In experiment 22 the gas flow to the second reactor ranged from an hourly space velocity of 10,000 to 14,700 volumes an hour per volume of catalyst. In

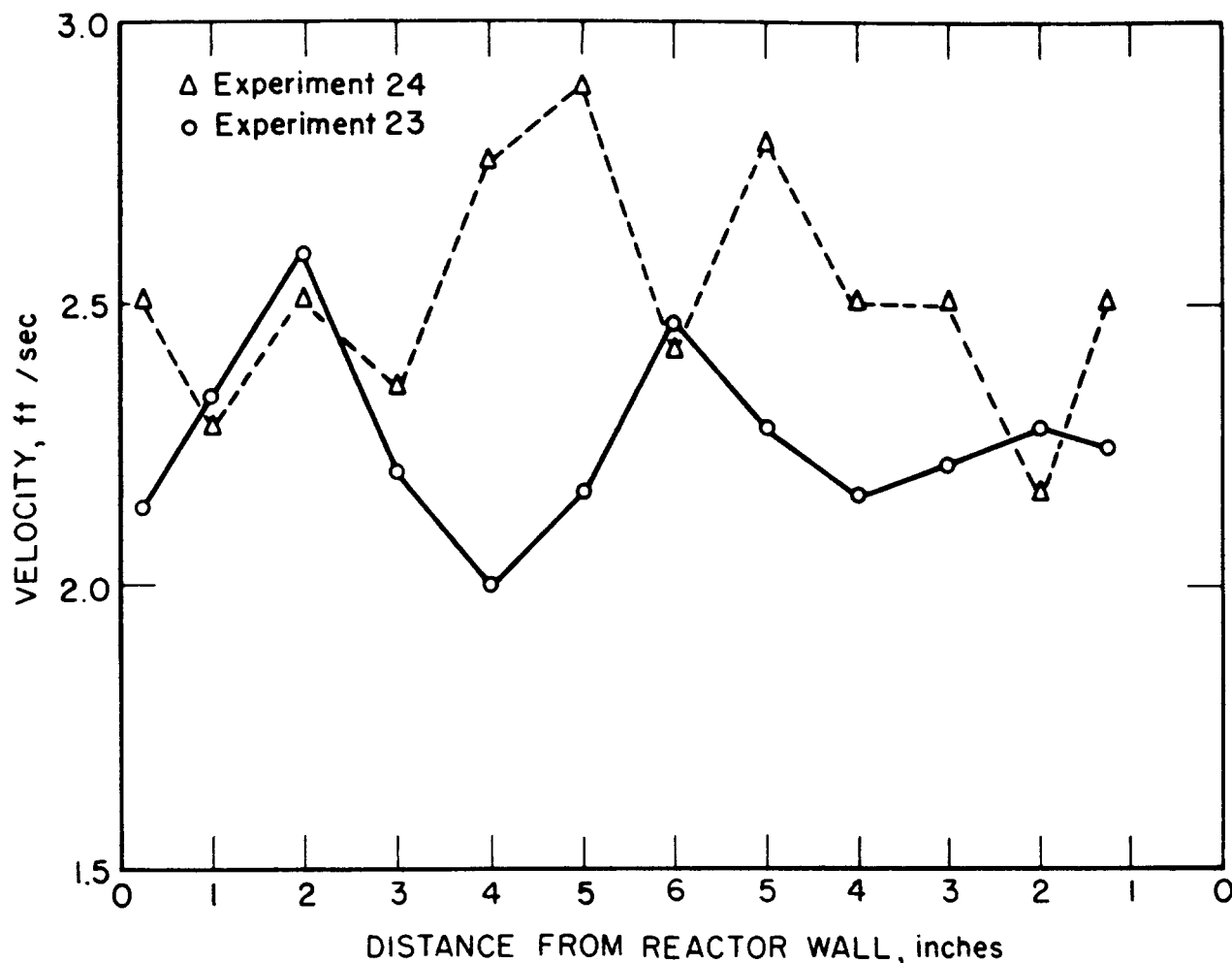


FIGURE 12. - Velocity Profiles Before Synthesis in Experiments 23 and 24.

period D (table 2) at a space velocity of 10,000 (28,000 vol/vol/hr based on first reactor feed)⁸ the overall H_2+CO conversion was 98.3 percent, and the calorific value of the product gas was 971 Btu per cubic foot. In period F at a feed rate of 14,700 (36,300 based on first reactor feed) the overall H_2+CO conversion was 83.8 percent, and the heating value was 791. A lower conversion is expected at the higher flow, but the lower conversion is at least partly due to the lower conversion in the first reactor. Although not shown in the table, in period D the H_2+CO conversion in the first reactor was 80.6 and in period F was 75.3 percent. Before period I the second reactor was placed in service, but the catalyst seemed to be completely inactive. The catalyst was therefore removed and analyzed both by chemical and X-ray diffraction methods, showing a high sulfur content. Table 3 shows analyses of the raw, charged, and discharged catalyst.

$$^{8} 10,000 = \frac{\text{volume of gas to second reactor per hour}}{\text{catalyst volume of second reactor}};$$

$$28,000 = \frac{\text{volume of fresh feed gas per hour}}{\text{catalyst volume of second reactor}}.$$

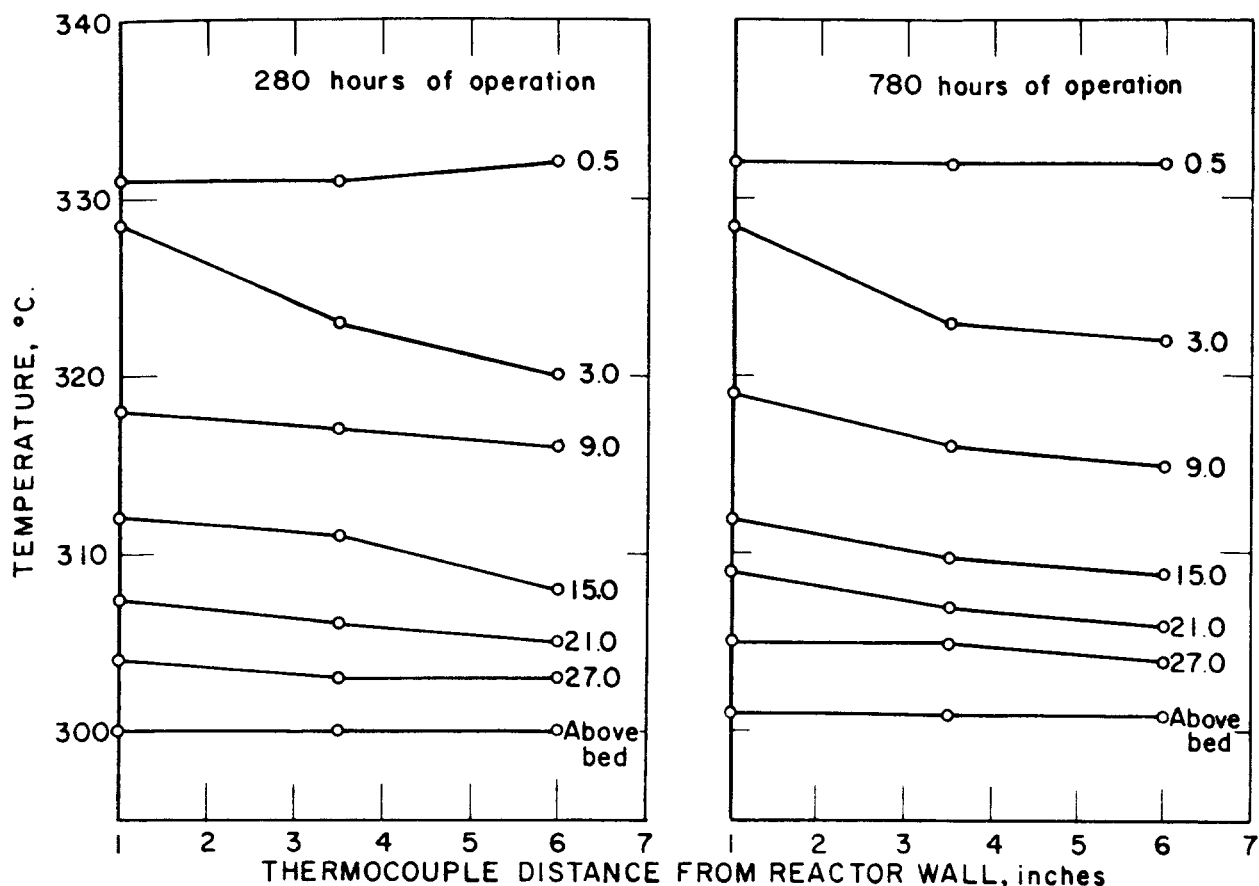


FIGURE 13. - Temperature Gradients in Catalyst Bed, Experiment 24.

The high sulfur content of the discharged catalyst, especially of the fines would explain the inactivity of the catalyst. A likely source of sulfur was the cylinder of commercial hydrogen used to blanket the catalyst during periods when the second reactor was not on stream. Analysis of this hydrogen showed 0.025 grain of sulfur per 100 cubic feet of hydrogen. The iron in the discharged catalyst may have come from the walls of the steel reactor. X-ray diffraction analysis of the fines showed AlNi , Ni , Fe_3O_4 , and Al_3Ni as the phases present.

A more satisfactory high-Btu gas was made in experiment 23 with a fresh charge of Raney nickel in the second reactor. The second reactor was operated at a gas flow of 9,100 vol/vol/hr. The $\text{H}_2 + \text{CO}$ conversion was 82.5 percent with the first reactor and 99.5 percent with both reactors. The calorific value of the product gas was 985 Btu per cubic foot, and the methane content was 94.3 percent. In addition to methanating the carbon monoxide, most of the carbon dioxide was reacted, and the heavier hydrocarbons were cracked and hydrogenated to methane. For example, in experiment 23 (table 2) the carbon dioxide, ethane, and propane were 7.6, 5.4 and 3.0 percent, respectively, in the tail gas of No. 1 reactor in period B. After the second reactor was placed in service in period C these components decreased to 1.3, 0.7, and 0.3 percent. These reactions are discussed in more detail in a previous report.⁹

⁹First work cited in footnote 4.

TABLE 2. - Operating conditions and results, experiments 22 and 23

Period.....	Experiment 22									Experiment 23		
	A	B	C	D	E	F	G	H	I	A	B	C
Synthesis.....hours	80-128	200-248	272-368	536-608	612-660	730-802	831-879	938-962	996-1,020	183-281	408-450	475-571
Main reactor conditions:												
Space velocity.....vol/vol/hr	851	851	849	854	848	849	852	852	1,000	704	711	706
Reactor pressure.....psig	403	405	405	406	406	403	403	405	405	405	404	398
Recycle to fresh feed ratios:												
Total.....	22	22	22	21	21	21	21	28	21	27	27	27
Hot.....	20	20	20	20	20	20	20	20	20	25	25	25
Cold.....	2	2	2	1	1	1	1	8	1	2	2	2
Reactor temperature, °C:												
In gas.....	300	300	299	300	300	300	300	300	300	290	301	299
Out gas.....	332	332	331	330	331	331	333	324	335	321	334	331
Increment.....	32	32	32	30	31	31	33	24	35	31	33	32
Average catalyst temperature.....°C	321	320	319	323	331	337	339	338	345	308	318	317
Maximum catalyst temperature.....°C	353	351	354	452	456	496	460	445	464	344	346	345
Catalyst pressure drop												
.....inches of H ₂ O/foot	8	8	8	8	8	8	10	10	10	6	6	6
Water vapor in recycle gas												
.....volume-percent	7.9	7.7	7.4	11.6	11.8	10.0	9.3	2.3	7.4	7.9	7.9	7.6
H ₂ :CO ratio, fresh gas.....	2.97	2.94	2.95	2.94	3.02	3.00	3.02	2.96	2.96	2.85	2.80	2.85
H ₂ :CO ratio, recycle gas.....	31.2	23.1	24.0	24.9	14.3	23.6	10.1	6.2	8.1	43.3	32.6	31.7
Second reactor conditions:												
Space velocity												
.....volume per volume per hour	-	-	10,000	10,000	10,700	14,700	-	-	-	-	-	9,100
Space velocity (based on fresh feed).....do.	-	-	30,900	28,000	31,600	36,300	-	-	-	-	-	26,000
Recycle to fresh feed ratio.....	-	-	8	7	7	7	-	-	-	-	-	7
Reactor temperature, °C:												
In gas.....	-	-	299	299	299	299	-	-	-	-	-	291
Out gas.....	-	-	351	349	350	350	-	-	-	-	-	350
Average catalyst temperature.....°C	-	-	321	328	328	326	-	-	-	-	-	320
Maximum catalyst temperature.....°C	-	-	351	349	350	350	-	-	-	-	-	350
Water vapor in recycle gas												
.....volume-percent	-	-	2.3	3.2	3.5	2.7	-	-	-	-	-	2.9
Overall results:												
Reactors in service.....	1	1	2	2	2	2	1	1	1	1	1	2
CO ₂ -free contraction.....percent	69.9	69.6	76.4	78.6	75.2	69.3	57.8	65.7	56.6	70.3	68.0	76.1
H ₂ conversion.....do.	79.8	78.7	99.1	97.8	96.1	85.7	64.8	74.8	60.0	77.3	76.9	99.3
CO conversion.....do.	98.1	97.3	99.9	99.9	99.2	98.2	89.4	88.0	85.3	98.5	98.0	99.9
H ₂ +CO conversion.....do.	84.4	83.4	99.3	98.3	96.9	83.8	70.9	78.2	66.4	82.9	82.5	99.5
H ₂ :CO ratio, usage.....	2.42	2.38	2.92	2.88	2.93	2.62	2.19	2.51	2.08	2.23	2.20	2.83
Heating value of tail gas ¹												
.....Btu/cu ft	766	720	986	971	949	791	573	639	484	705	713	985
Tail gas composition, volume-percent: ²												
H ₂	46.8	48.6	2.8	7.5	11.4	33.0	57.5	52.3	62.9	52.0	48.9	2.1
CO.....	1.5	2.1	0.1	0.1	0.8	1.4	5.7	8.4	7.8	1.2	1.5	0.1
N ₂	1.1	0.5	0.8	0.7	0.8	0.8	0.6	0.6	0.8	0.9	0.9	1.1
CO ₂	6.2	6.8	1.4	1.4	2.0	5.2	8.2	4.2	8.4	7.5	7.6	1.3
C ₁	32.1	31.9	93.5	87.4	80.8	53.6	21.4	27.3	16.2	27.4	30.8	94.3
C ₂	0	0	0	0	0	0	0	0	0	0	0	0
C ₃	6.4	5.4	0.9	1.9	2.7	3.3	3.5	3.9	2.1	5.6	5.4	0.7
C ₄	0.3	0.2	0.1	0.1	0.1	0.2	0.3	0.2	0.1	0.3	0.3	0.1
C ₅	3.6	2.9	0.3	0.7	1.0	1.6	1.8	1.9	0.9	3.4	3.0	0.3
C ₆	0.2	0.2	0	0	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0
C ₇	1.4	1.1	0.1	0.2	0.2	0.6	0.5	2.7	0.4	1.2	1.0	0
C ₈	0	0	0	0	0	0	0.1	0	0.1	0	0.1	0
C ₉	0.4	0.3	0	0	0.1	0.2	0.2	0.3	0.1	0.3	0.3	0
Feed gas per cubic foot tail gas.....cubic feet	3.11	3.07	4.17	4.61	3.95	3.09	2.18	2.79	2.11	3.11	2.88	4.13
Tail gas ³do.	547	555	407	370	430	550	782	610	947	452	493	342
Yield, grams per cubic meter of H ₂ +CO converted:												
H ₂	89	89	162	137	151	149	98	90	82	75	92	163
CO.....	0	0	0	0	0	0	0	0	0	0	0	0
C ₁	34	29	3	6	10	17	31	24	20	29	31	2
C ₂	2	1	1	0	1	1	4	2	1	2	2	0
C ₃	28	23	1	3	5	13	24	18	13	26	25	2
C ₄	2	2	0	0	1	1	3	2	4	2	2	0
C ₅	15	4	1	0	1	6	9	9	8	12	11	0
C ₆	0	0	0	0	0	0	2	0	2	0	1	0
C ₇	5	7	0	0	1	3	4	5	2	4	4	0
C ₈	7	7	4	4	5	3	5	5	3	10	6	4
Oil.....	194	187	189	184	196	204	165	214	150	193	192	192
Aqueous.....	1	1	0	0	0	1	1	4	2	2	2	11
C-C ₂ OH ⁴	0	0	0	0	0	0	0	0	0	0	0	0
Other oxygenates ⁴	193	186	189	184	196	203	164	210	148	191	190	181
Water.....	47	50	7	6	10	40	105	36	119	57	61	6
CO ₂												
Hydrocarbon recovery												
.....grams per cubic meter	183	163	172	150	175	194	181	159	137	160	174	171
Theoretical recovery.....do.	188	189	181	185	182	190	187	193	192	191	190	181

¹ Cubic feet corrected to 60° F and 30 inches of mercury (dry).² Dry basis.³ Corrected to ° C and 760 millimeters of mercury.⁴ Calculated as hydrocarbons.

TABLE 3. - Raney nickel catalyst analyses, weight-percent

	Raw	Charge	Discharge	
			Coarse	Fines ¹
Aluminum.....	-	42.9	-	-
Nickel.....	40.4	51.37	-	-
Sodium.....	0	.029	0.003	0.08
Carbon.....	.01	.17	.34	1.96
Sulfur.....	.035	-	.103	.52
Iron.....	-	-	2.55	29.0

¹Through 20-mesh screen.

In experiment 24 with the same charge of Raney nickel as used in experiment 23, the hydrogen concentration increased and the methane concentration decreased as the experiment progressed (fig. 14, and table 4, period B). Apparently the activity of the Raney catalyst had decreased. This decrease may have been due to the high space velocity (11,000 vol/vol/hr) employed and to the age of the catalyst (over 1,000 hr). However, the product gas still had a satisfactory heating value, above 900 Btu per cubic foot, after 950 hours of service (fig. 14). At this time the carbon monoxide content of the gas was 0.1 percent, and the olefin content was 0.2 to 0.3 percent.

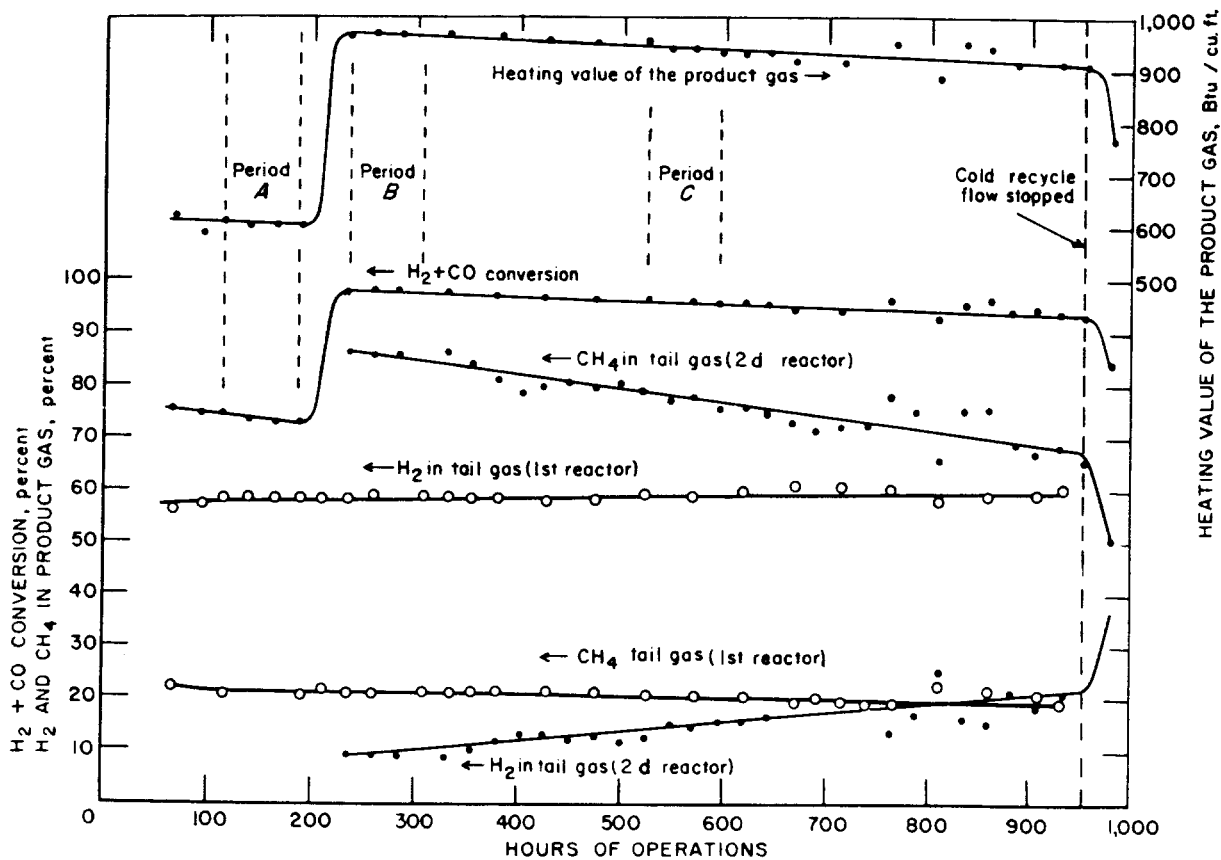


FIGURE 14. - Feed Gas Conversion, Calorific Values, and Hydrogen and Methane Content of Tail Gas During Experiment 24.

TABLE 4. - Operating conditions and results, experiment 24

Period.....	A	B	C
Synthesis.....hours	115-187	221-283	499-571
Main reactor conditions:			
Space velocity.....vol/vol/hr	706	704	704
Reactor pressure.....psig	405	402	406
Recycle to fresh feed ratio:			
Total.....	26	26	26
Hot.....	25	25	25
Cold.....	1	1	1
Reactor temperature, ° C:			
In gas.....	300	300	300
Out gas.....	331	331	330
Increment.....	31	31	30
Average catalyst temperature.....° C	315	315	314
Maximum catalyst temperature.....° C	334	334	333
Catalyst pressure drop.....inches of H ₂ O/foot	7	7	8
Water vapor in recycle gas.....volume-percent	11.4	9.7	9.8
H ₂ :CO ratio, fresh feed.....	3.01	2.94	2.89
H ₂ :CO ratio, recycle gas.....	23.3	21.2	14.0
Second reactor conditions:			
Second reactor space velocity.....vol/vol/hr	-	11,200	11,500
Second reactor space velocity (based on first reactor feed).....	-	30,700	30,700
Recycle to fresh feed ratio.....	-	5.9	6.1
Reactor temperature, ° C:			
In gas.....	-	279	274
Out gas.....	-	350	350
Average catalyst temperature.....° C	-	311	308
Maximum catalyst temperature.....° C	-	350	350
Water vapor in recycle gas.....volume-percent	-	3.9	3.8
Overall results:			
Reactors in service.....	1	2	2
CO ₂ -free contraction.....percent	59.9	74.9	73.7
H ₂ conversion.....do.	65.2	97.0	94.9
CO conversion.....do.	95.5	99.9	99.9
H ₂ +CO conversion.....do.	72.8	97.7	96.2
H ₂ :CO ratio, usage.....	2.05	2.86	2.75
Heating value of tail gas ¹Btu/cu ft	603	969	942
Tail gas composition, volume-percent: ²			
H ₂	58.5	8.8	13.9
CO.....	2.5	0.1	0.1
N ₂	0.4	0.7	0.7
CO ₂	9.6	1.4	2.5
C ₁	20.7	85.6	77.8
C ₂	-	-	-
C ₃	4.1	2.2	3.0
C ₄	0.2	0.1	0.2
C ₅	2.5	0.7	1.3
C ₆	0.2	0.1	0.1
C ₇	0.9	0.3	0.4
C ₈	0.1	-	-
C ₉	0.3	-	-
Feed gas per cubic foot tail gas.....cubic feet	2.25	3.92	3.71
Tail gas ³do.	626.1	358.9	379.7
Yield, grams per cubic meter of H ₂ +CO converted:			
H ₂	90.0	160.3	155.8
C ₁	-	-	-
C ₂	34.2	7.8	11.4
C ₃	2.4	0.6	1.1
C ₄	31.1	3.7	7.3
C ₅	3.3	0.8	0.8
C ₆	14.8	2.2	3.0
C ₇	1.9	-	-
C ₈	6.3	-	-
Oil.....	5.6	1.9	2.6
Aqueous.....	183.1	198.7	205.2
C ₂ -C ₃ OH ⁴	2.3	0.8	2.0
Other oxygenates ⁴	0	0	0
Water.....	180.8	197.9	203.2
CO ₂	105.6	5.2	11.8
Hydrogen recovery.....grams per cubic meter	189.6	177.3	182.0
Theoretical recovery.....do.	188.0	181.0	181.1

¹Cubic feet corrected to 60° F and 30 inches of mercury (dry). ³Corrected to 0° C and 760 millimeters of mercury.²Dry basis.⁴Calculated as hydrocarbons.

The Raney nickel previously used in experiments 23 and 24 was reused in experiment 25. As shown in table 5, in period C, an overall conversion of 91.2 percent was obtained when operating at a feed rate of 12,600 vol/vol/hr at a catalyst temperature of 327° C average. The calorific value of the product gas was 871 Btu. Increasing the temperature (period D) to an average of 341° C did not improve the heating quality of the off gas, even though the methane content increased.

This catalyst was then removed from the second reactor and replaced by two plate assemblies made of Raney nickel. After the catalyst was activated, the second reactor was put on stream at a space velocity of feed gas of 12,600 vol/vol/hr (period E); temperature averaged 326° C. The overall conversion of H₂+CO was 92.2 percent. The inlet temperature was 290° C; the outlet, 350° C, and between the sections, 340° C. This indicates about 80 percent of the reaction occurred in the top 6-inch section. At a higher average temperature of 366° C (period F, table 5), the conversion was 89.9 percent. The plates were as active as the granular Raney nickel used previously in the same experiment, but not as active as a fresh charge of granular catalyst.

Synthesis of Gasoline

Experiment 26 was made to study the synthesis of liquid fuels in the 12-inch-diameter reactor. Several modifications were made in the pilot plant: The second reactor system was removed as it is not required when liquids are produced; the carbon dioxide scrubbing system used in earlier experiments¹⁰ was reactivated to treat the cold recycle gas. Figure 15 shows a flowsheet of the pilot plant for the synthesis of liquid hydrocarbons.

An alkalized catalyst of lathe turnings was charged to the 12-inch-diameter reactor. After reduction, synthesis with gas composed of 1.4H₂+1CO was started in the same manner as previous experiments. Steady-state conditions for period A were as follows:

Fresh gas.....	1.4H ₂ +1CO
Fresh gas rate...std cu ft/hr	¹ 1,410
Recycle-to-fresh feed ratio:	
Total.....	22
Hot.....	20.5
Cold.....	1.5
Reactor temperature, ° C:	
Inlet.....	290
Outlet.....	326
Maximum.....	333
Average.....	309
H ₂ +CO conversion.....	² 75.5
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¹ 705 vol/vol/hr.	
² Percent.	

¹⁰Second work cited in footnote 4.

TABLE 5. - Operating conditions and results, experiment 25

Period.....	A	B	C	D	E	F	G	H	I	J
Synthesis.....hours	54-78	121-217	265-361	433-481	625-721	769-841	865-913	961-985	1,009-1,057	1,081-1,153
Main reactor conditions:										
Space velocity.....vol/vol/hr	702	700	704	702	707	707	701	709	705	705
Reactor pressure.....psig	403	402	401	400	404	404	403	402	401	402
Recycle to fresh feed ratios:										
Total.....	27	26	26	26	26	26	27	27	26	26
Hot.....	26	25	25	25	25	25	25	25	25	25
Cold.....	1	1	1	1	1	1	2	2	1	1
Reactor temperatures, ° C:										
In gas.....	299	300	300	300	300	300	299	300	300	320
Out gas.....	331	330	330	330	329	327	324	327	327	351
Increment.....	32	30	30	30	29	27	25	27	27	31
Average catalyst temperature.....° C	315	315	315	316	315	315	313	315	317	340
Maximum catalyst temperature.....° C	335	336	336	336	335	335	334	345	363	392
Catalyst pressure drop.....inches of H ₂ O/foot	7	7	7	7	7	7	7	7	7	7
Water vapor in recycle gas.....volume-percent	11.5	10.7	10.3	9.8	9.4	8.9	6.2	6.4	8.7	10.0
H ₂ :CO ratios:										
Recycle gas.....	27.6	22.2	13.8	13.9	10.2	8.6	8.8	8.6	10.6	13.4
Fresh feed.....	2.93	2.99	2.98	2.87	2.93	2.94	2.91	3.07	3.04	2.98
Second reactor conditions:										
Second reactor space velocity.....vol/vol/hr	-	-	12,600	12,600	12,600	12,600	-	13,900	6,000	4,500
Second reactor space velocity (based on first reactor feed).....	-	-	30,700	30,700	30,700	30,700	-	30,900	13,400	10,000
Recycle to fresh feed ratio.....	-	-	6	4	8	4	-	4	5	5
Reactor temperatures, ° C:										
In gas.....	-	-	300	301	290	299	-	299	296	294
Out gas.....	-	-	361	401	350	398	-	400	400	400
Average catalyst temperature.....° C	-	-	327	341	326	366	-	363	363	361
Maximum catalyst temperature.....° C	-	-	361	401	350	398	-	400	400	400
Water vapor in recycle gas.....volume-percent	-	-	4.2	6.0	3.4	6.0	-	4.8	5.7	6.8
Overall results:										
Reactor in service.....	1	1	2	2	2	2	1	2	2	2
CO ₂ -free contraction.....percent	64.2	62.4	73.0	72.9	71.7	70.0	55.0	72.7	69.1	68.5
H ₂ conversion.....do.	71.0	68.1	88.3	91.4	89.2	87.3	64.0	90.0	89.8	91.4
CO conversion.....do.	96.9	95.7	99.7	99.1	98.1	97.7	88.0	97.0	97.9	98.4
H ₂ +CO conversion.....do.	77.6	75.1	91.2	93.4	92.2	89.9	70.1	91.7	91.8	93.2
H ₂ :CO ratio, usage.....	2.15	2.13	2.64	2.65	2.66	2.63	2.11	2.85	2.78	2.76
Heating value of tail gas ¹Btu/cu ft	640	692	871	875	842	793	570	817	831	851
Tail gas composition, volume-percent: ²										
H ₂	55.1	57.7	31.0	22.6	24.6	30.0	58.9	26.6	23.8	19.5
CO.....	2.0	2.6	0.3	0.8	1.6	1.9	6.7	2.6	1.6	1.2
H ₂ O.....	0.4	0.4	0.7	0.7	0.7	0.7	0.4	0.7	0.7	0.7
CO ₂	8.5	8.9	4.3	3.9	4.0	4.4	7.0	3.8	4.2	4.2
C ₁	24.2	22.7	53.1	65.9	64.5	58.9	20.2	62.1	66.3	70.8
C ₂	0	0	0	0	0	0	0	0	0	0
C ₃	4.8	4.1	5.6	3.7	2.6	2.2	3.7	2.4	1.8	2.0
C ₄	0.6	0.3	1.3	0.3	0.2	0	0.1	0.1	0.1	0.3
C ₅	3.1	2.3	2.8	1.6	1.2	1.5	2.2	1.3	1.2	0.9
C ₆	0.2	0.1	0	0.1	0.1	0	0.1	0	0	0.1
C ₇	1.0	0.7	0.8	0.4	0.4	0.3	0.6	0.3	0.2	0.3
C ₈	0.1	0	0.1	0	0	0	0	0	0	0
C ₉	0	0.2	0	0	0.1	0.1	0.1	0.1	0.1	0
Feed gas per cubic foot tail gas.....cubic feet	2.56	2.42	3.54	3.55	3.39	3.18	2.20	3.53	3.10	3.04
Tail gas ³do.	548	577	397	396	417	444	637	402	455	464
Yield, grams per cubic meter of										
H ₂ +CO converted:										
H ₂	89	90	118	143	149	148	94	138	165	180
CO.....	0	0	0	0	0	0	0	0	0	0
C ₁	33	31	23	15	11	11	33	10	9	10
C ₂	6	3	8	2	1	0	1	1	1	2
C ₃	32	26	18	10	8	11	29	9	9	7
C ₄	3	2	0	8	1	0	2	0	0	1
C ₅	10	10	7	3	4	3	11	3	2	3
C ₆	2	0	1	0	0	0	0	0	0	0
C ₇	0	4	0	0	1	1	2	1	1	0
Oil.....	5	5	2	2	2	1	4	2	1	2
Aqueous.....	184	181	198	192	192	192	181	197	208	202
C ₁ +C ₂ OH ⁴	-	1	-	0	1	1	2	-	0	1
Other oxygenates ⁴	-	0	-	0	0	0	0	-	0	0
Water.....	-	180	-	192	191	191	179	-	208	201
CO ₂	86.1	98	24	23	23	28	90	23	29	11
Hydrocarbon recovery.....grams per cubic meter	180	171	176	183	176	174	173	164	188	205
Theoretical recovery.....do.	189	189	186	183	186	182	188	184	185	202

¹Cubic feet corrected to 60° F and 30 inches of mercury (dry).²Dry basis.³Corrected to 0° C and 760 millimeters of mercury.⁴Calculated as hydrocarbons.

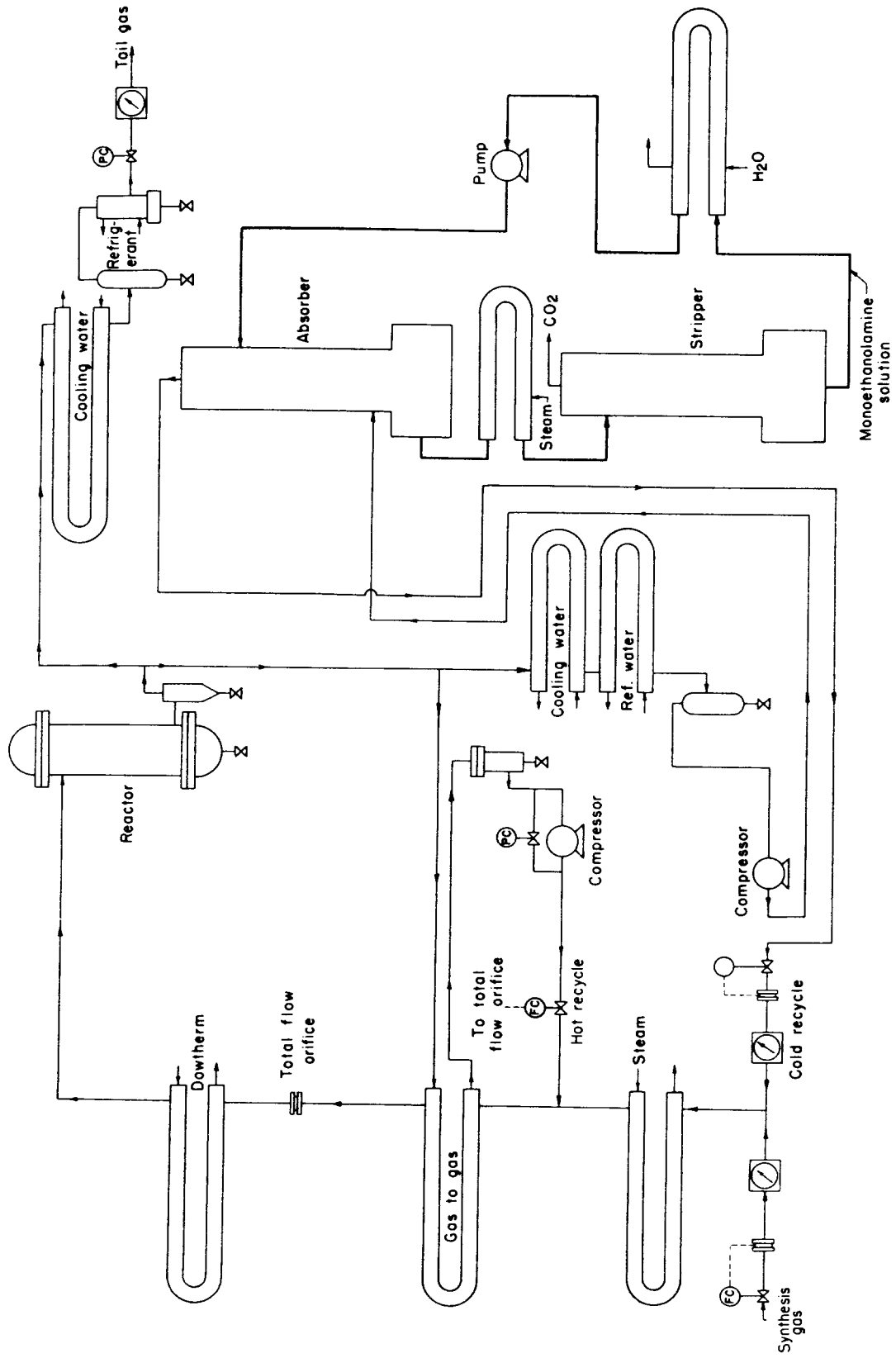


FIGURE 15. - Hot-Gas-Recycle Flowsheet for the Production of Gasoline.

Other conditions of operation and results are shown in table 6. The space velocity of feed gas was then lowered to about 600 vol/vol/hr to raise the gas conversion. The plant was operated for over 800 hours at these conditions. A series of tests was then made to find the effect of temperature on product distribution. The reactor had been operating at an average temperature of 307° C. Additional steady-state periods were maintained at 275°, 291°, 325°, and 338° C. While the average temperature was 325° C, a hotspot developed in the bottom of the reactor near the wall. After the 338° C period, the unit was shut down. Experiment 26 was operated for a total of 1,102 hours. Carbon was found in the bottom 9 inches of the bed when the catalyst was removed.

DISCUSSION OF RESULTS

General

The purpose of these experiments was to demonstrate good temperature control when operation of the hot-gas-recycle process, using a 12-inch-diameter reactor, was prolonged. This purpose was realized in experiments 24 through 26.

The success of these three experiments may be attributed to the improved gas distribution resulting from the method of charging the catalyst and a maximum catalyst temperature maintained below 340° C.

The catalyst was charged to give a maximum linear velocity at the center of the bed. The effectiveness of this method of packing is shown by the smaller radial temperature gradients in experiments 24 and 25 compared with experiments 22 and 23. Early in experiment 23 (fig. 11), the maximum differential between wall and center temperatures on the same level in the catalyst was 25° C. In experiment 24 (fig. 13), this difference was only 8° C; in experiment 25 (fig. 16), only 9° C; in experiment 26 (fig. 17), about 14° C.

The packing was not, however, the only factor. In experiment 24, after 800 hours, a deliberate increase in the maximum temperature of the bottom of the catalyst bed from 328° to 350° C caused a hotspot to develop, and since the bed temperatures could not be controlled, the experiment was ended. In experiment 25, after 865 hours of successful operation, when the cold recycle-to-fresh feed ratio was increased from 1 to 2, a hotspot again developed. Again in experiment 26 after 1,000 hours when the temperature of the catalyst bed was increased, hotspots developed.

Before experiments 24 through 26 started, velocity profiles were taken to determine the condition of catalyst packing. If the gas distribution was poor, the catalyst was dumped and recharged.

TABLE 6. - Operating conditions and results, experiment 26

Period.....	A	B	C	D	E	F	G	H
Synthesis.....hours	128-176	200-272	416-488	672-744	864-912	924-972	988-1,032	1,060-1,096
Reactor conditions:								
Space velocity.....vol/vol/hr	705	606	607	605	504	505	802	799
Reactor pressure.....psig	403	405	405	401	402	402	404	406
Recycle to fresh feed ratios:								
Total.....	22	26	27	30	31	31	23	24
Hot.....	20.5	24.5	25.5	28.5	29.5	29.5	21.5	22.5
Cold.....	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
CO ₂ scrubbed.....	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Reactor temperature, °C:								
In gas.....	290	290	289	290	260	275	305	319
Out gas.....	326	322	321	317	283	300	339	345
Increment.....	36	32	32	27	23	25	34	26
Average catalyst temperature.....°C	309	308	308	307	275	291	325	338
Maximum catalyst temperature.....°C	333	328	328	323	288	305	348	355
Catalyst pressure drop.....inches of H ₂ O/foot	6	6	6	9	7	7	10	17
H ₂ :CO ratio, fresh gas.....	1.43	1.44	1.45	1.42	1.40	1.38	1.40	1.39
Results:								
CO ₂ -free contraction.....percent	70.7	75.6	74.6	70.5	53.7	63.0	74.0	79.2
H ₂ conversion.....do.	69.9	74.4	73.7	68.7	50.2	60.2	73.3	81.0
CO conversion.....do.	83.4	90.0	88.7	86.0	67.5	77.9	87.9	94.0
H ₂ +CO conversion.....do.	75.5	80.8	79.8	75.8	57.4	67.7	79.4	86.6
H ₂ :CO ratio:								
Recycle gas.....	2.59	3.68	3.35	3.17	2.15	2.46	3.07	4.30
Usage.....	1.20	1.19	1.21	1.13	1.04	1.07	1.17	1.19
Water vapor in recycle gas.....volume-percent	6.2	7.1	7.0	6.2	3.7	5.0	6.8	8.7
Heating value of tail gas ¹Btu/cu ft	491	562	536	505	393	431	522	655
Tail gas composition, volume-percent: ²								
H ₂	56.1	56.6	55.2	56.1	57.4	56.3	52.2	45.2
CO.....	21.7	15.4	16.5	17.7	26.7	22.9	17.0	10.5
N ₂	1.5	0.9	1.2	0.8	1.2	1.2	1.2	1.2
CO ₂	6.8	8.0	9.6	9.7	8.0	9.5	12.3	14.7
C ₁	7.9	10.0	9.8	8.0	3.6	5.0	8.3	15.6
C ₂	0.8	1.3	0.7	1.1	0.6	0.7	1.5	1.3
C ₃	1.1	2.5	2.3	1.8	0.7	1.1	1.8	3.1
C ₄	0.9	1.3	0.3	2.3	0.2	1.5	2.9	3.6
C ₅	0.2	0.7	1.0	0.6	0	0.3	0.5	1.1
C ₆	1.7	0.6	0.6	1.0	0.5	0.8	1.4	1.9
C ₇	0.4	2.0	1.8	0.3	0.3	0.4	0.3	0.5
C ₈	0.4	0.2	0.2	0.4	0.1	0.3	0.5	0.9
C ₉	0.5	0.5	0.8	0.1	0.7	0	0.1	0.2
C ₁₀	0	0	0	0.1	0	0	0	0.2
C ₁₁	0	0	0	0	0	0	0	0
Yield, grams per cubic meter of H ₂ +CO converted:								
C ₁	23	22	24	24	23	22	22	31
C ₂	4	5	3	6	7	7	7	5
C ₃	7	11	12	11	9	15	9	12
C ₄	7	8	2	19	3	24	21	20
C ₅	2	5	7	5	0	8	4	6
C ₆	18	5	6	12	12	16	14	14
C ₇	6	18	18	4	8	10	4	5
C ₈	6	2	2	6	3	6	6	8
C ₉	7	6	9	1	22	0	1	2
C ₁₀	0	0	0	2	0	0	0	2
C ₁₁	0	0	0	0	0	0	0	0
Oil.....	101	96	97	98	119	100	95	84
Aqueous.....	123	128	130	125	113	119	133	134
C ₁ -C ₃ OH ³	7	9	8	7	5	7	7	5
Other oxygenates ³	3	3	3	3	1	2	3	2
Water.....	113	116	119	115	107	110	123	127
CO ₂	323	306	307	315	353	324	294	284
Hydrocarbon recovery.....grams per cubic meter	191	190	191	198	212	217	193	196
Theoretical recovery.....do.	203	202	201	201	203	202	203	201
Hydrocarbon recovered, weight-percent:								
C ₁ +C ₂	16.8	18.8	19.4	20.4	18.4	20.2	18.7	23.9
C ₃	1.0	2.5	3.5	2.5	0	3.7	2.0	3.0
Gasoline (C ₅ = - 204° C).....	60.9	58.8	59.0	58.9	49.0	46.7	62.4	59.7
Diesel oil (204° - 316° C).....	10.7	10.2	9.1	9.2	10.2	5.6	9.3	8.8
Fuel oil (316° - 450° C).....	7.4	6.3	6.2	6.0	9.8	8.3	5.0	3.3
Wax (<450° C).....	3.2	3.4	2.8	3.0	12.6	15.5	2.6	1.3

¹ Cubic foot corrected to 60° F and 30 inches of mercury (dry).² Dry basis.³ Calculated as hydrocarbons.

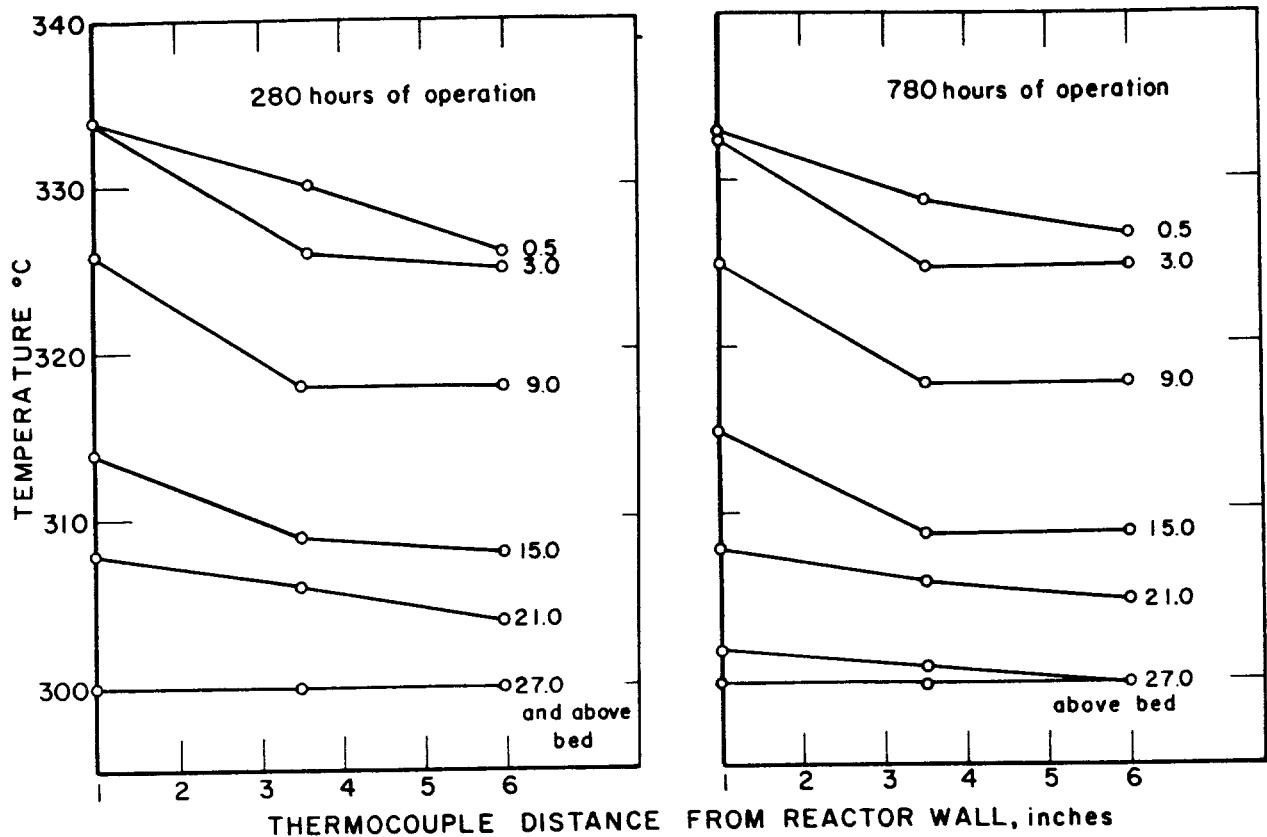


FIGURE 16. - Temperature Gradients in Catalyst Bed, Experiment 25.

To maintain the desired temperature differential in a commercial reactor using the hot-gas-recycle process the linear velocity of the gas was estimated to be 3 to 4 feet per second if a 10-foot bed height were used. In the experimental 12-inch reactor, because gas supply and compression equipment were limited, a linear velocity of 1 foot per second was used. The difficulties in operating the 12-inch-diameter reactor were largely attributed to the low linear velocity of the gas. By operating at a velocity of about 1 foot per second instead of 3 feet per second, the heat transfer coefficient, which varies with the 0.8 power of the velocity, is decreased about 60 percent. When distribution of gas is uneven as a result of packing the catalyst, the velocity of the gas will be less than the 1 foot per second in certain places, and the heat transfer rate will be decreased even further. As a result, heat removal is inadequate with the formation of localized hotspots and the deposition of carbon. The carbon particles aggravate the difficulty by impeding heat transfer and flow of gas.

High-Btu Gas Experiments

Single Reactor with Steel Lathe Turnings

The same degree of gas conversion was obtained in the 12-inch diameter reactor as in the 3-inch. In experiment 18,¹¹ period J, the H₂+CO conversion

¹¹First work cited in footnote 4.

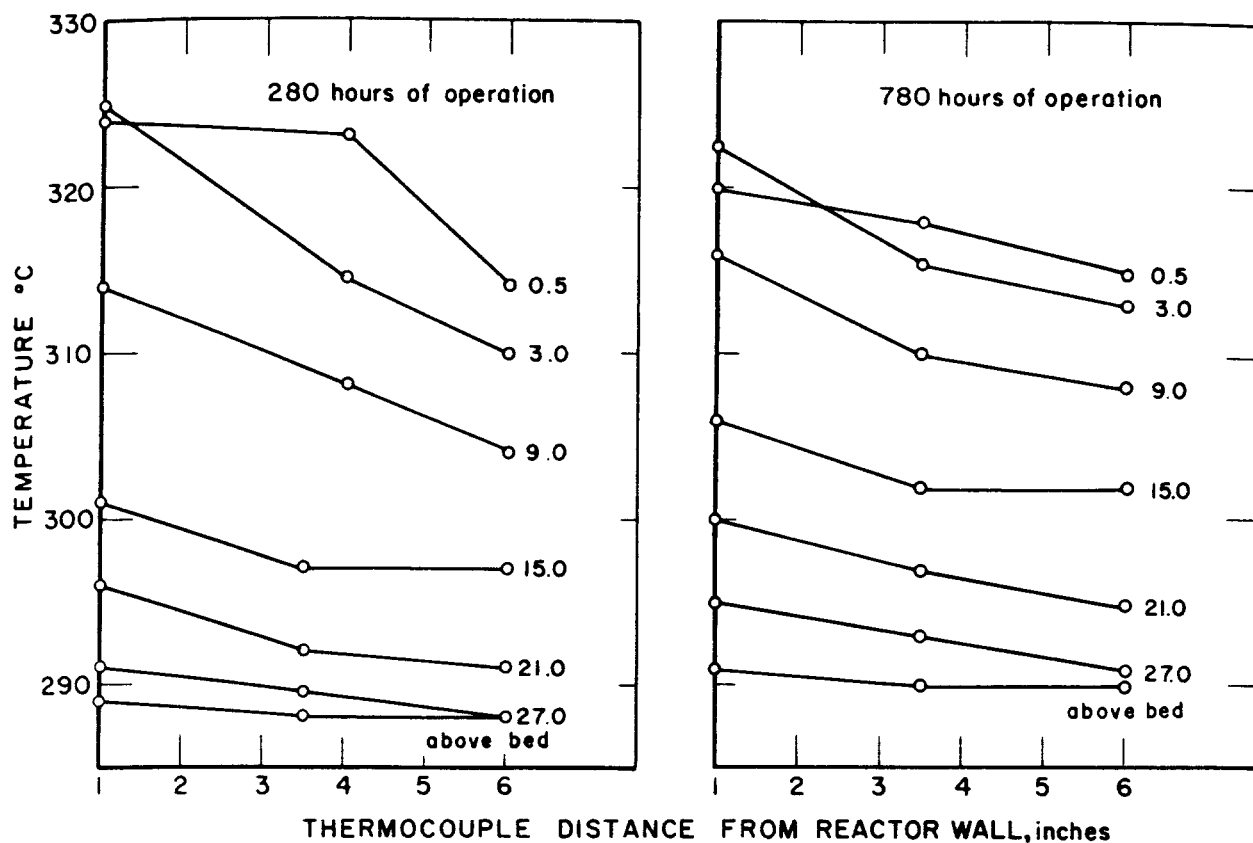


FIGURE 17. - Temperature Gradients in Catalyst Bed, Experiment 26.

was 85.3 percent at a synthesis gas rate of 802 vol/vol/hr at an average of 319° C catalyst temperature, compared with 84.4 percent at 851 vol/vol/hr at 321° C in experiment 22, period A (table 2). The calorific value of the gas was similar--741 Btu in experiment 18, period J, compared with 766 Btu per cubic foot in experiment 22, period A.

Two Reactors in Series

The use of Raney nickel catalyst in a second reactor to upgrade the product of the first reactor has been described in a previous report.¹² The purpose of operating with two reactors in the present experiments was twofold: To operate the second reactor using only recycle gas to remove the exothermic heat of reaction, and to use a shape of Raney nickel with less resistance to gas flow than the commercially available granular material.

In previous experiments¹³ the bed temperatures in the second reactor were controlled by the combination of boiling Dowtherm in the jacket of the reactor and cold recycle gas. In the experiments reported here, however, only cold recycle gas was used (fig. 1). The water vapor content of the recycle gas in

¹² First work cited in footnote 4.

¹³ First work cited in footnote 4.

the second reactor is 2 to 4 percent (table 2). This low figure is due to operating with a cold recycle compressor. If a hot compressor were used, the water vapor content would be higher.

The temperature control in the second reactor system was very good. No hotspots developed, and the temperature was controlled as desired by recycling 7 to 8 volumes of recycle gas for each volume of feed to the second reactor. This low recycle rate was possible because the feed gas to the second reactor is not pure synthesis gas.

The maximum conversion of the fresh feed with both reactors in service was 99.5 percent. In period C, experiment 23, it was 99.5 percent at 9,100 volumes of feed gas per hour to the second reactor per volume of its catalyst. In period B of experiment 24 (table 4), it was 97.7 percent at 11,200 vol/vol/hr. In experiment 25, period D, (table 5) it was 93.4 percent at 12,600. The lower conversion obtained in experiment 25 was probably due more to catalyst age than to the higher feed rate. The same catalyst charge was used in experiments 23 through 25. The catalyst had operated for more than 1,200 hours when it was dumped; over 30,000 cubic feet of methane was produced per pound of catalyst during this total time.

Pressure Drop

In the main reactor pressure drop per foot of catalyst height in these experiments was 6 to 10 inches of water. This pressure drop could not be extrapolated to indicate that of a commercial-size reactor since the geometry of the reactor would be entirely different. This reactor had a bed height of 3 feet, but a commercial reactor may be 10 to 20 feet high. At the same space velocity, the linear velocity varies directly with bed height, and the pressure drop varies with the 1.9 power of the velocity.¹⁴ Other factors, such as density of packing and deposition of carbon, affect the overall pressure drop.

In the second reactor the pressure drop through the bed of granular particles was about 17 inches of water per foot of height, and for the plate assemblies it was about 1.5 inches. Conditions of operation were approximately the same for both catalysts. The pressure drop in the second reactor therefore was reduced 90 percent by using the parallel plate assemblies rather than the granules of Raney nickel. Pressure drop significantly affects the cost of recompressing the recycle gas.

Gasoline Experiment

Experiment 26 was undertaken to demonstrate the operation of the 12-inch reactor for the synthesis of gasoline as well as high-Btu gas. By packing the catalyst in the reactor carefully, as discussed previously in experiment 24, the plant was operated successfully; good temperature control was maintained for over 1,000 hours.

¹⁴Jimeson, R. M., and W. A. Decker. Pressure-Drop Measurements Through Beds of Granular Iron, Lathe Turnings, Steel Wool, and Parallel Plate Assemblies. BuMines Rept. of Inv. 5541, 1959, 51 pp.

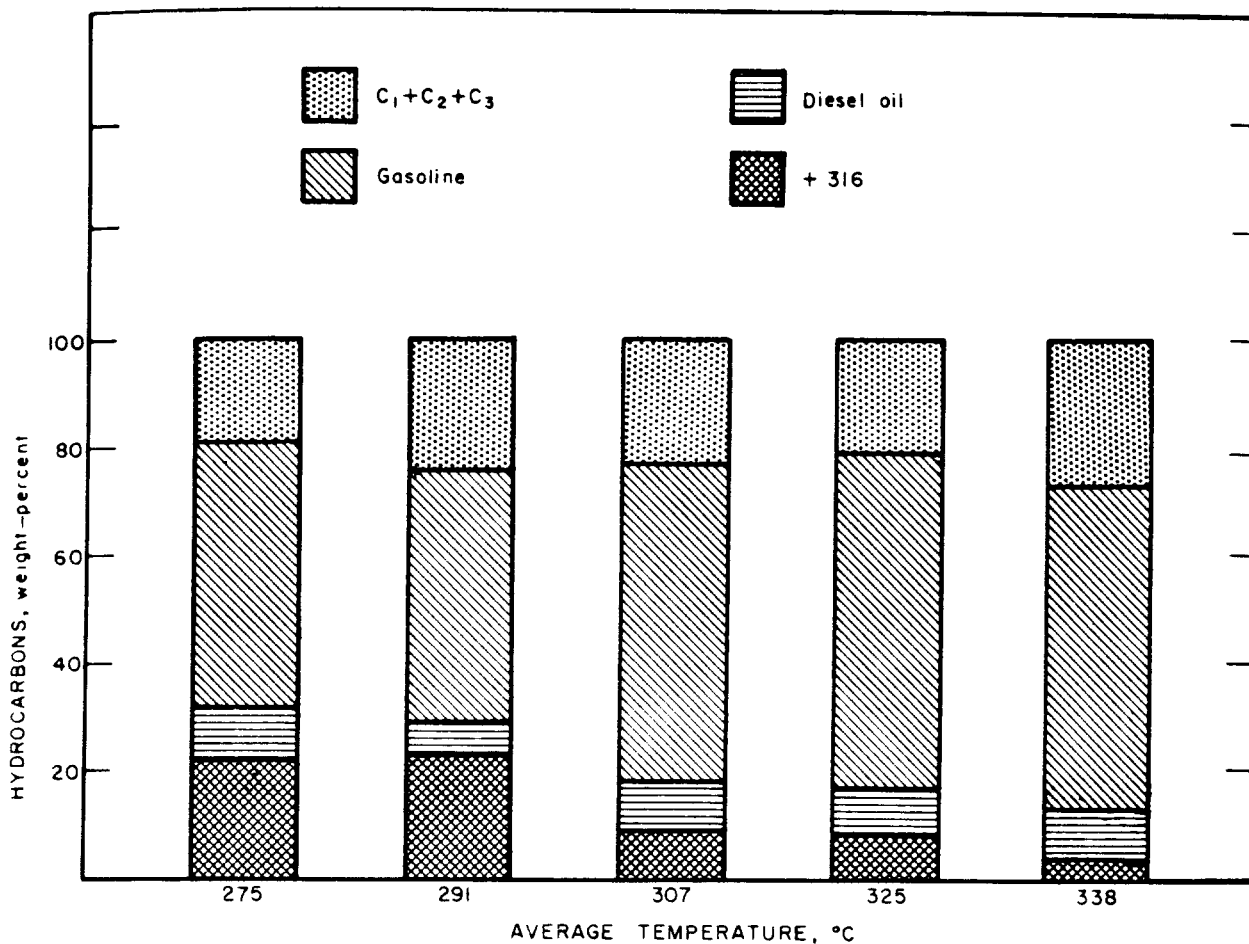


FIGURE 18. - Effect of Catalyst Temperature on Product Distribution.

A study was made of the product distribution resulting from varying the average bed temperature from 275° to 338° C. The space velocity was also varied because of operational requirements, but previous experiments have shown that this has little effect on product distribution. Figure 18 shows the results of this study. As the average temperature was increased from 275° to 325° C, the percentage of gasoline increased and the heavier hydrocarbons decreased. From 325° to 338° C, the gasoline yield decreased slightly. Earlier experiments¹⁵ showed that the gasoline yield decreased as the temperature was increased from 353° to 390° C. Above 325° C the gasoline is probably cracking. These results would indicate the temperature for maximum gasoline production would be about 325° C.

Catalysts and Catalyst Activity

Table 7 shows X-ray analyses of catalyst samples taken from the top of the bed at intervals during experiments 21 to 26. Experiment 21 was made in the 3-inch-diameter reactor¹⁶ with alkaliized turnings. The data for

¹⁵ Second work cited in footnote 4.

¹⁶ First work cited in footnote 4.

experiment 21 are included to allow a comparison of alkalized turnings in the small and large reactors. Only the outer active surface of the turnings is analyzed. In experiment 21 the alpha iron formed during reduction was converted to Hägg carbide during the synthesis. Experiments 22 to 25 showed some Hägg carbide to be present, but not as a major phase. Instead, considerable Fe_3O_4 was present, even though it is only a minor phase after reduction. Experiment 26 shows only Hägg carbide, the same as experiment 21. The presence of Hägg carbide may be related to the fact that both catalysts were alkalized. This finding agrees with that of Pichler.¹⁷ The catalyst seems to be as active when the surface is predominantly alpha iron and Fe_3O_4 as it is when the surface is predominantly Hägg Fe_2C . In experiment 18¹⁸ Period J, the H_2+CO conversion was 85.3 percent at a fresh gas feed of 802 vol/vol/hr at 319° C, compared with 83.4 percent conversion at 320° C at a feed of 851 vol/vol/hr in experiment 22, period B. Periods in experiments 23 through 25 where the surface was alpha Fe and Fe_3O_4 primarily, indicate equal activity, compared with experiment 26 where the surface was Hägg Fe_2C (tables 2-6).

TABLE 7. - X-ray analysis of catalyst¹

Hours	Expt. 21 ²	Hours	Expt. 22 ³	Hours	Expt. 23 ³
0.....	αFe Fe_3C^4	0.....	αFe	0.....	αFe
290.....	Hägg Fe_2C	600.....	αFe	404.....	Fe_3O_4
530.....	Hägg Fe_2C		Fe_3O_4		αFe
912.....	Hägg Fe_2C	1,100.....	Hägg Fe_2C		Fe_3O_4
1,268.....	Hägg Fe_2C		αFe	718.....	Hägg Fe_2C
1,500.....	Hägg Fe_2C		Fe_3O_4		αFe
1,920.....	Hägg Fe_2C		Hägg Fe_2C		Fe_3O_4
					Hägg Fe_2C
Hours	Expt. 24 ³	Hours	Expt. 25 ³	Hours	Expt. 26 ²
0.....	αFe	0.....	αFe	0.....	αFe
	Fe_3O_4		Fe_3O_4		Fe_3O_4^4
336.....	αFe	217.....	αFe	320.....	Hägg Fe_2C
	Fe_3O_4		Fe_3O_4	488.....	Hägg Fe_2C
	Hägg Fe_2C		Hägg Fe_2C	625.....	Hägg Fe_2C
888.....	αFe	365.....	αFe	1,102.....	Hägg Fe_2C
	Fe_3O_4		Fe_3O_4		
	Hägg Fe_2C	513.....	αFe		
		940.....	Fe_3O_4		
			αFe		
			Fe_3O_4		
			Hägg Fe_2C		

¹Major phase presented first.

²Alkalized.

³Non-alkalized.

⁴Trace only.

¹⁷Pichler, Helmut. Twenty-Five Years of Synthesis of Gasoline by Catalytic Conversion of Carbon Monoxide and Hydrogen: Advances in Catalysts. Ed. by W. G. Frankenburg, V. I. Kavarensky, and E. K. Rideal. Academic Press, Inc., New York, N.Y., v. 4, 1952, p. 333.

¹⁸First work cited in footnote 4.

In experiment 23, 1,948 grams of Raney nickel catalyst, which had been activated by caustic treatment, was charged to the reactor. Only 1,531 grams of used catalyst was dumped after a total of 1,248 hours of operation in experiments 23 through 25. Analysis indicated 331 grams of nickel had been lost. As the average production of methane was estimated at 135 standard cubic feet per hour, slightly less than 2 grams of nickel (5 grams Raney nickel) were lost per 1,000 standard cubic feet of high-Btu gas produced. Based on a price of Raney nickel of \$0.90 per pound, the catalyst cost \$0.01 per 1,000 standard cubic feet of gas produced, including activation costs.

CONCLUSIONS

A 12-inch-diameter reactor used in the hot-gas-recycle process has been shown to be operative in the synthesis of gaseous and liquid fuels. Early difficulties were introduced by limitations of equipment when working with a superficial linear velocity of 1 foot per second, whereas the 3-inch-diameter reactor used previously was operated with a velocity of 3 to 4 feet per second. This low linear velocity caused poor distribution of gas and resulted in localized overheating and deposition of carbon in the catalyst bed. By changing the technique in charging the catalyst to the reactor, higher gas velocities were achieved in the center of the bed. Better control of heat and longer life of catalyst were then obtained. It may be concluded that when packing is evenly distributed a linear velocity of less than 1 foot per second does not result in effective temperature control. When packing is less evenly distributed, higher linear velocities are required at the expense of increased pressure drop. The cost spent in obtaining various degrees of even packing distribution must be balanced against the expense of the pressure differential produced by the linear velocity that is required to maintain temperature control of the particular packing distribution.

Raney nickel proved to be an excellent methanation catalyst in the second-stage reactor to convert the remaining hydrogen and carbon monoxide, to hydrogenate carbon dioxide, and to crack and to hydrogenate higher hydrocarbons in the product gas from the first reactor. A change in the form of Raney nickel catalyst from granules to plates reduced the pressure drop through the second reactor by 90 percent. Catalyst activity decreased slightly, however.

With carbon steel turnings as catalyst, 84-percent conversion of the feed gas was obtained at an hourly space velocity of 850. The heating value of the product gas was 750 Btu per cubic foot. On sending the product gas to a second reactor with Raney nickel as catalyst, 99 percent conversion was obtained, and the heating value of the product gas was 986 Btu per cubic foot.

When the catalyst was alkalized steel turnings 104 grams of gasoline per cubic meter of H_2+CO converted (49 percent of the hydrocarbon yield) was obtained at 275° C. This production was increased to 171 grams per cubic meter (62 percent of the hydrocarbon yield) as the temperature was raised to 325° C. Above 325° C the gasoline yield declined, and the yield of gaseous hydrocarbons increased.

The foregoing figures demonstrate the versatility of the process. The production can be adjusted to produce from 99 percent high-Btu gas to 80 percent liquid hydrocarbon yields.