

effects of space velocity on the distribution of product and heating values of the product gases are summarized in figures 20, 21, and 22.

To prevent carbon deposition, carbon dioxide and steam were added to the synthesis-gas feed. When a synthesis gas containing 5 percent CO_2 was used with catalyst D-3001, the quantity of carbon deposited was not reduced; whereas, when steam was added to the synthesis gas in quantities greater than 2.6 percent, carbon deposition was prevented. The addition of steam, however, adversely affected the activity of the catalyst, and no activity could be observed when 27-percent steam was added to the synthesis-gas feed. The activity of the catalyst was partly restored as the steam concentration was decreased. Even with small amounts of steam, however, the activity of the catalyst was much lower than in the absence of steam and the recycle ratio had to be increased to maintain the activity at a level equivalent to that obtained with no steam addition. Table 4 is a comparison of the results obtained with and without steam addition at various recycle ratios, and at a temperature, pressure, and total space velocity of 340°C ., 300 p.s.i.g., and 7,200 hr^{-1} , respectively.

TABLE 4. - Effects of recycle ratio and steam addition at constant total space velocity

Catalyst: D-1034						
Composition: Scrap steel fines, reduced and nitrided						
H_2/CO : 2.5:1						
Total space velocity, fresh feed plus recycle: 7,200 hr^{-1}						
Temperature: 340°C .						
Steam addition, percent by volume of fresh feed	0	0	0	2.6	2.6	
Recycle ratio	1:1	2:1	3:1	3:1	4:1	
H_2+CO conversion	percent	57.3	67.9	74.7	69.1	79.5
Product gas analysis, percent by volume:						
CH_4	12.7	18.2	24.1	19.6	26.7	
C_2H_6	2.92	3.85	4.67	3.75	5.49	
CO_2	9.70	10.6	11.0	11.8	12.1	
H_2	61.3	55.8	50.1	55.2	48.6	
CO	11.4	9.14	7.66	7.59	3.97	
$\text{C}_3 +$ - hydrocarbon yield, gm. per cu. m.	12.3	8.97	12.0	8.06	9.03	
Gross heating value, B.t.u. per cu. ft. (CO_2 , H_2O free) ..	532	604	627	608	723	
Calorific efficiency	49.6	57.5	63.4	57.8	65.0	

Discussion of Iron-Catalyst Tests in Conventional Bed

The iron catalysts were not active enough to produce an acceptable fuel gas without adding recycled product gases. In most instances, recycle ratios of about 3:1 were required to produce a gas having a heating value in the range of 700 B.t.u. per cu. ft. Generally, the gas was produced at low calorific efficiencies.

Although addition of steam inhibits the deposition of carbon, which is a major problem when iron catalysts are used, it also inhibits the activity of the catalyst, and, as a result, high recycle ratios are required to maintain the maximum conversion rates of synthesis gas.

The results of these tests with iron catalysts appear to verify the conclusions that were based on the fixed-bed tests. Since the yields of C_3+ hydrocarbons are high with iron catalysts, it would appear that the use of these materials for a process producing only methane would be impractical. Moreover, the deposition of carbon on iron catalysts appears to be an extremely difficult problem to solve.

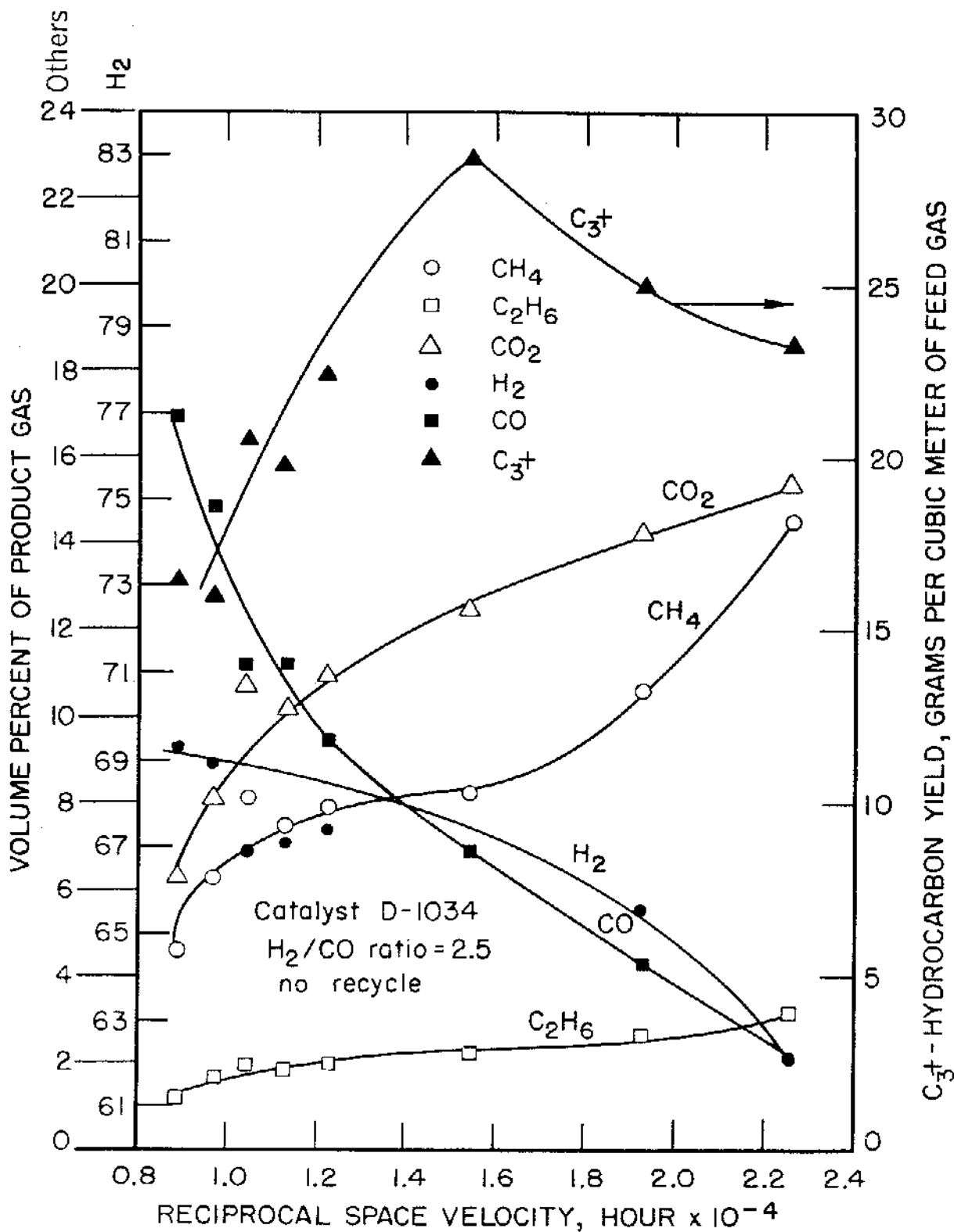
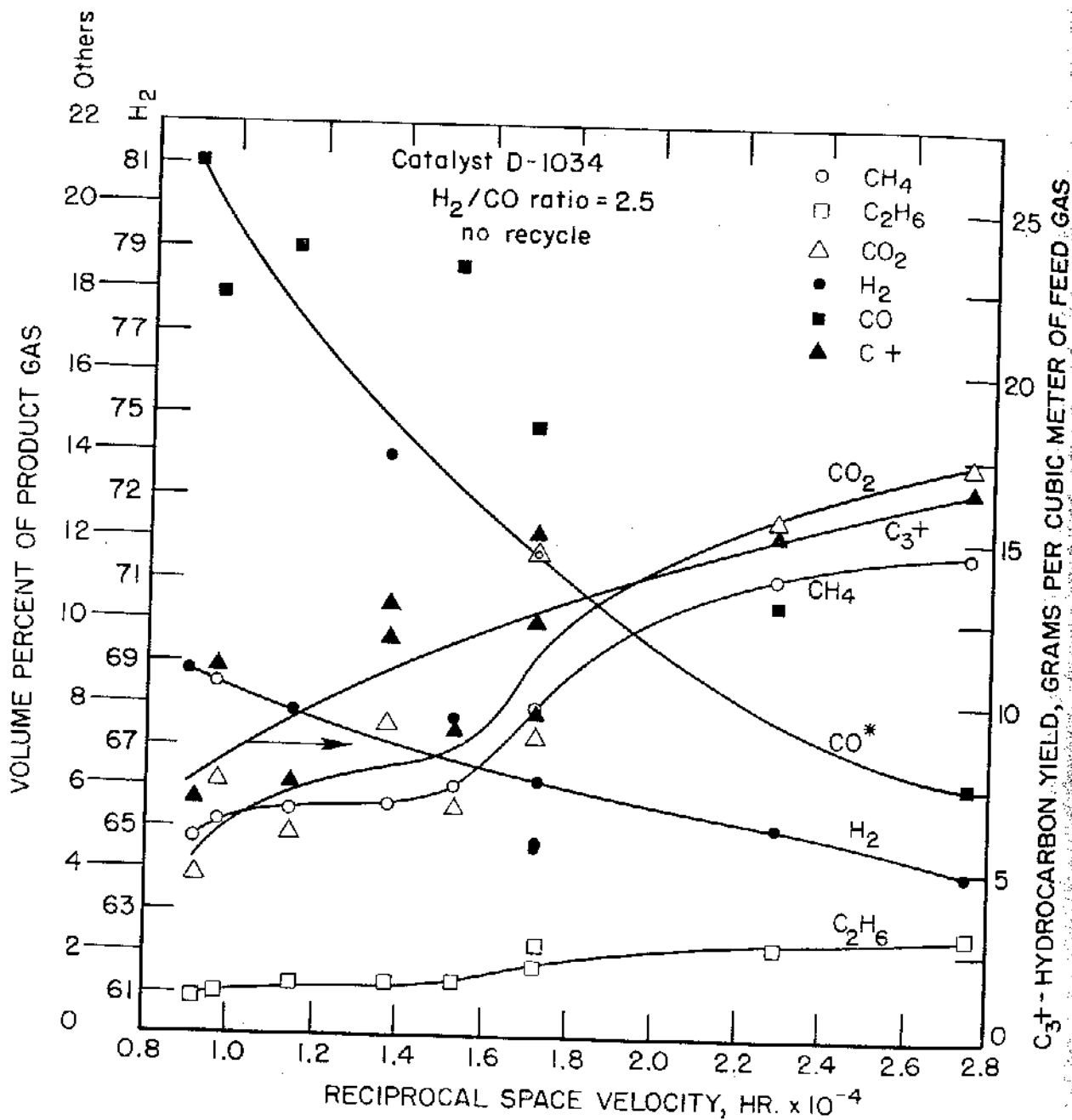


Figure 20. - Effect of space velocity on products; 340° C., 300 p.s.i.g.



* CO analyses inaccurate due to N_2 in gas samples.

Figure 21. - Effect of space velocity on products; $350^\circ C.$, 300 p.s.i.g.

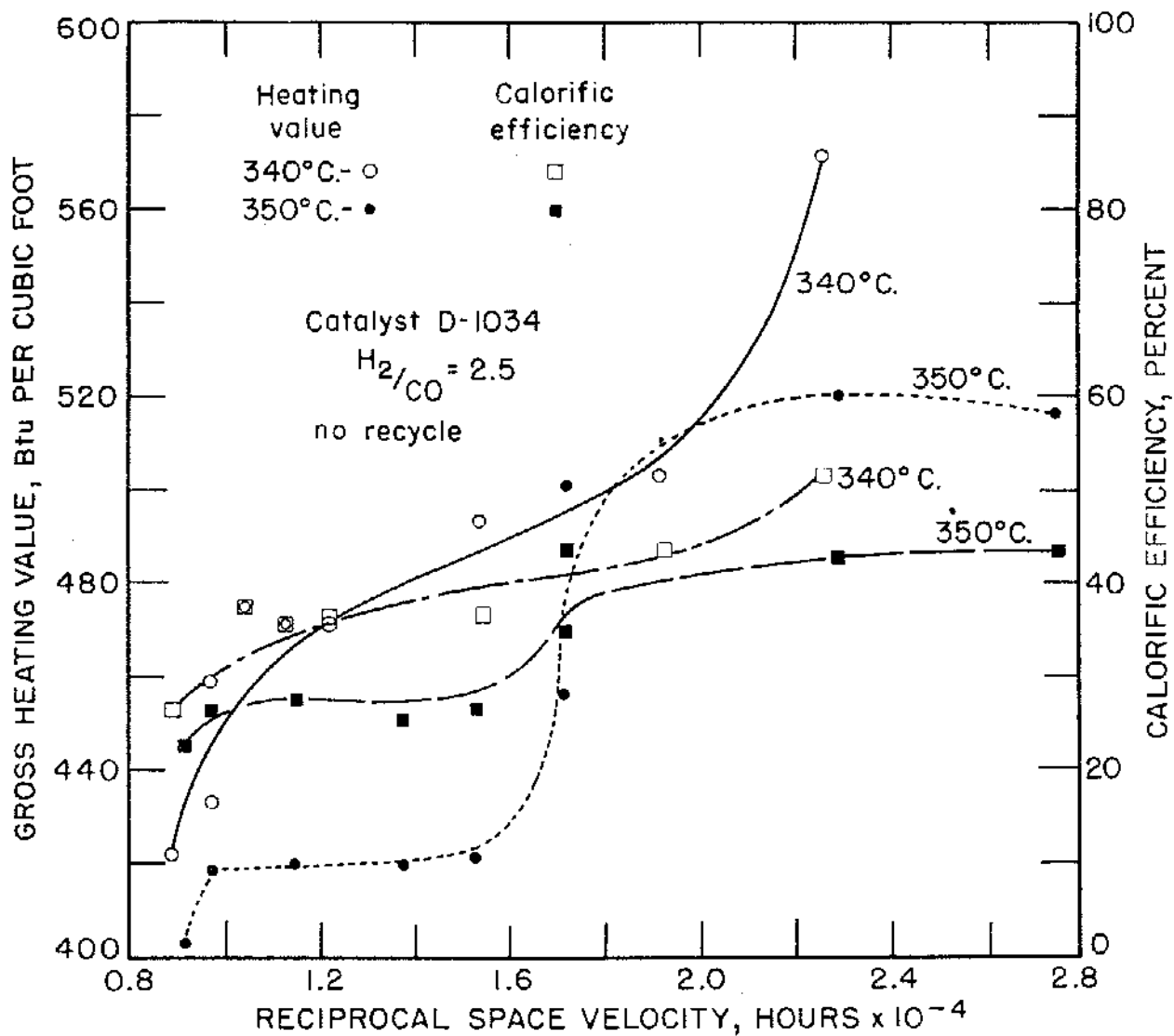


Figure 22. - Effect of space velocity on heating value and calorific efficiency; 300 p.s.i.g.

As was mentioned previously, however, iron might still be suitable for use in a combined process producing both gaseous and liquid products, and it is quite possible that such a process operated at a lower temperature might not be subject to the excessive amount of carbon deposition that was observed in these experiments.

Results and Discussion of Nickel-Catalyst Tests in Conventional Bed

The initial work with nickel catalyst was carried out in the conventional fluidized-bed reactor. The first 3 catalysts tested, 5-percent nickel impregnated on alumina (Girdler Catalyst, L-6016), 5-percent nickel impregnated on cracking-catalyst base (L-6014), and 10-percent nickel impregnated on crushed silica (L-6024), were found to be completely inactive through the temperature and pressure range 210°-400° C. and 0-300 p.s.i.g., respectively.

Since these results were in complete disagreement with those obtained in the fixed-bed work, the operating procedures in both systems were analyzed. It was found that the synthesis gas used in the fixed-bed operations was passed through an activated-charcoal trap before being admitted into the reactor, whereas the gas used in the fluidized-bed work was passed directly into the reactor from the high-pressure manifold. The additional purification that was obtained in the charcoal trap evidently decreased the sulfur concentration below 0.1 grain per M c.f. The actual effect of the trap, however, could not be determined, since the precision of the sulfur analyses made by this laboratory was only ± 0.05 grain per M c.f. It was thought that the difference between the sulfur concentrations in the synthesis gases used in the respective systems and the fact that a great deal of sulfur could have deposited on the catalysts during the initial temperature search might be responsible for the lack of agreement between the results obtained from each system. To prevent the sulfur from becoming an unknown variable in subsequent fluidized-bed work, a similar trap, which is shown in figure 18, was installed in the high-pressure manifold of the fluidized-bed system.

After the activated-charcoal trap was installed, a nickel-alumina-kaolin catalyst (L-6025, NiO:Al₂O₃: Kaolin = 100:159:97) was tested and was found to be extremely active. The catalyst was run for 65 hours at a space velocity of 5,530 hr.⁻¹, during which time a product gas having a heating value of better than 1,000 B.t.u. per cu. ft. was produced. At the end of 65 hours the space velocity was increased to 11,000 hr.⁻¹ and the heating value of the product gas remained essentially constant. After a total run time of 138 hours the activated-charcoal trap was bypassed, and shortly thereafter the activity of the catalyst began to decrease. At 184 hours after the initiation of synthesis, the run was terminated because of low catalyst activity. This test is summarized in table 5. Analysis of the catalyst after discharge revealed that the material contained 0.3 percent sulfur by weight.

Because the charcoal trap had been bypassed during the run, two more runs were made with this material with the trap in the system in order to evaluate the performance of the catalyst. Although the product-gas analyses and calorific efficiencies for both runs were very similar to the first run, the temperature of the reactor during the tests could not be controlled. At space velocities of less than 2,000 hr.⁻¹ and recycle ratios of greater than 2:1, temperature differences of over 100° C. were observed in the catalyst bed. During these runs it was observed that the highest temperatures in the catalyst bed always occurred 6 to 10 inches above the gas-inlet point.

TABLE 5. - Catalyst L-6025, conventional bed

Catalyst composition: NiO-Al₂O₃ - kaolin, 100:159:97

Pretreatment: Reduced with H₂ at 400° C. and 100 p.s.i.g. for 60 hours

H₂/CO ratio: 2.5

	1	2	3	4	5	6	7	8
Period	5,530	5,530	5,530	11,000	11,000	11,000	11,000	11,000
Fresh-feed space velocity, hr. ⁻¹	8	32	65	112	138	144	168	184
Catalyst age, end of period	hrs.							
Reactor temperature	°C.							
Reactor pressure	p.s.i.g.	300	304	300	300	300	300	300
Conversion H ₂ +CO	percent	98.0	97.7	99.9	99.4	95.5	95.3	85.2
Product gas analysis, (dry basis), percent by volume:								
C ₁		81.6	80.8	91.8	81.2	71.6	70.4	50.7
C ₁ +		0.00	0.00	0.00	0.00	0.00	0.06	0.48
CO ₂		11.6	11.9	14.2	14.5	13.6	14.1	8.70
H ₂		5.09	5.96	4.78	4.15	13.3	14.8	30.1
CO		1.32	1.38	1.18	2.14	0.78	0.06	10.1
Calorific efficiency	percent	99.9	99.9	99.9	95.0	90.5	90.3	75.2
Gross heating value, B.t.u. per cu. ft. (CO ₂ , H ₂ O free)		1,015	1,010	1,060	1,020	945	940	755

Charcoal trap bypassed after 138 hours.
No samples taken.

The catalyst was modified by reducing the nickel content to $1/3$ and then to $1/16$ of the original value, but the temperatures still could not be controlled. The support material in the catalyst was then changed from kaolin to crushed silica, but this procedure also failed to give temperature control of the reactor. By the time that the third catalyst had been tested, the excessive temperatures had severely damaged the reactor and replacement was necessary.

The tests conducted in this unit revealed that most of the heat of the reaction was being liberated in a relatively small zone about 6 to 8 inches above the gas inlet. This zone had insufficient heat-transfer area for effective control of the catalyst-bed temperatures, and, as a result, synthesis gas flow rates had to be decreased, and recycle ratios increased to maintain bed temperatures at a safe operating level.

Multiple-Feed Bed

General

The second unit that was built differed from the original conventional unit in that the gas that was fed to the reactor was divided into three separate streams and each stream was admitted to the reactor at a different bed height.^{25/} This feed system was designed to distribute the reaction throughout the tube and to minimize the localized heating observed in the original unit. It was also believed that, since all the synthesis gas that was admitted at a level would be completely converted before the next higher inlet was reached, the product gases from each inlet point would act as a diluent gas for the synthesis gas being admitted at the next higher level. Provision was also made in this design to permit the introduction of recycle gas at any one or all of the feed-gas inlet points, if necessary.

Equipment Description

The multiple-feed fluidized-bed unit is shown schematically in figure 23. The unit is almost identical in design with the conventional unit, except for a slight increase in the sizes of various components. The reactor consists of a 1-inch, Schedule 80, seamless steel pipe 6 feet in length enclosed in a 3-inch, Schedule 40, heat-exchanger jacket. The thermocouple well and baffle tube for this unit is a $3/8$ -inch-diameter steel tube. The 3 gas-inlet points for the reactor are located at the bottom, 18 inches above the bottom, and 36 inches above the bottom of the reactor. Carryover of catalyst particles with the product gas and settling of catalyst particles into the flange section of the unit are prevented in the same manner as in the conventional unit.

The flow system for the unit is shown in figure 24. The synthesis-gas stream, after passing through an activated-charcoal trap, pressure-reducing valve, and rotameter, is divided into three streams by throttle valves, which control the flow of gas to the various inlet points. The bottom gas stream follows a path that is identical with the feed-gas flow in the original unit. The two upper feed-gas streams are introduced through tubes that run down through the jacket of the reactor in which the gas is preheated and they are then passed directly into the side of the reactor tube.

The product-gas system is identical with that of the conventional unit, except that the recycle-gas stream is divided after passing through the rotameter. Three

^{25/} Patent procedures covering this type of reactor design have been initiated.

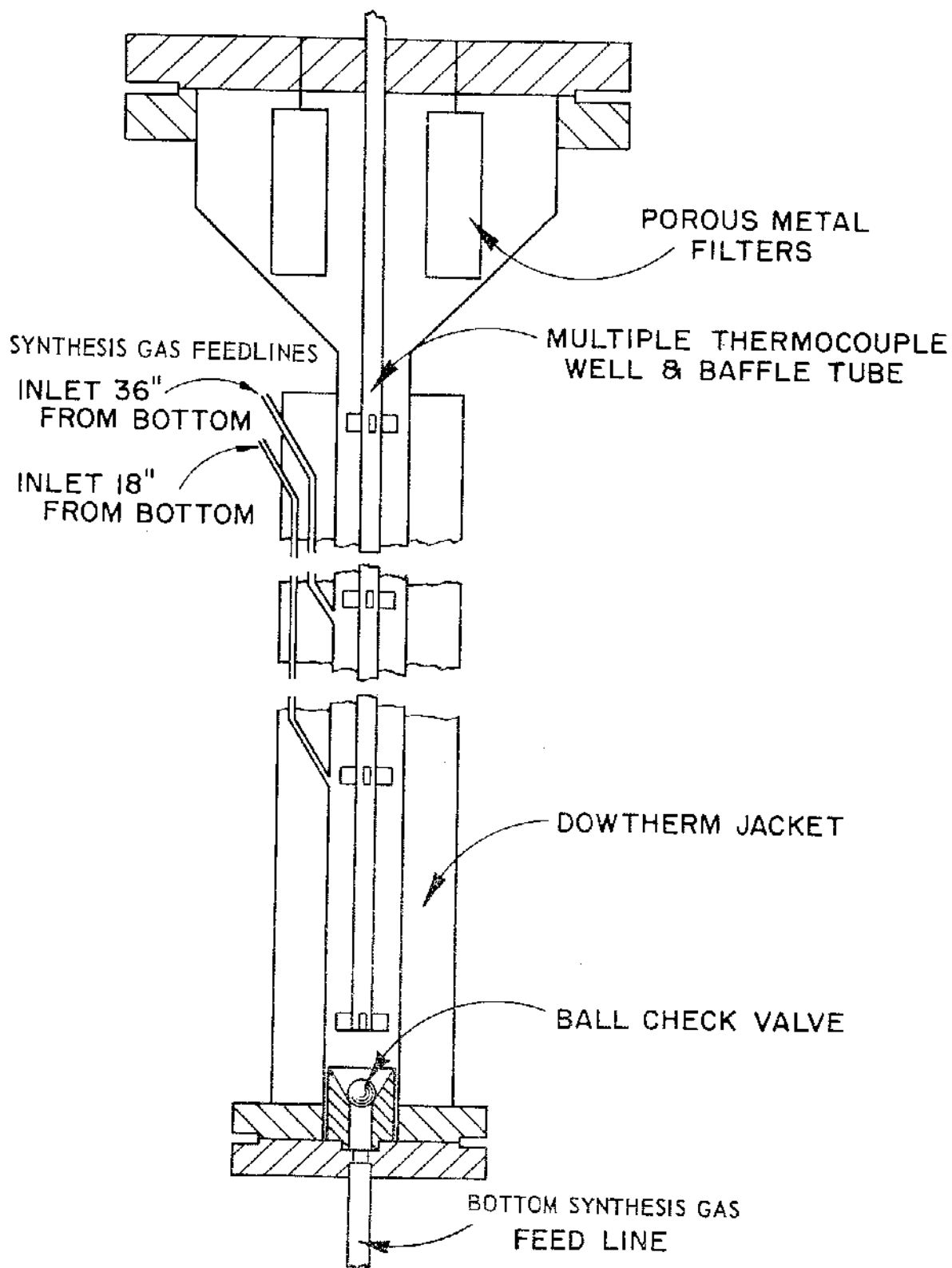


Figure 23. - Multiple-feed, fluidized-catalyst reactor.

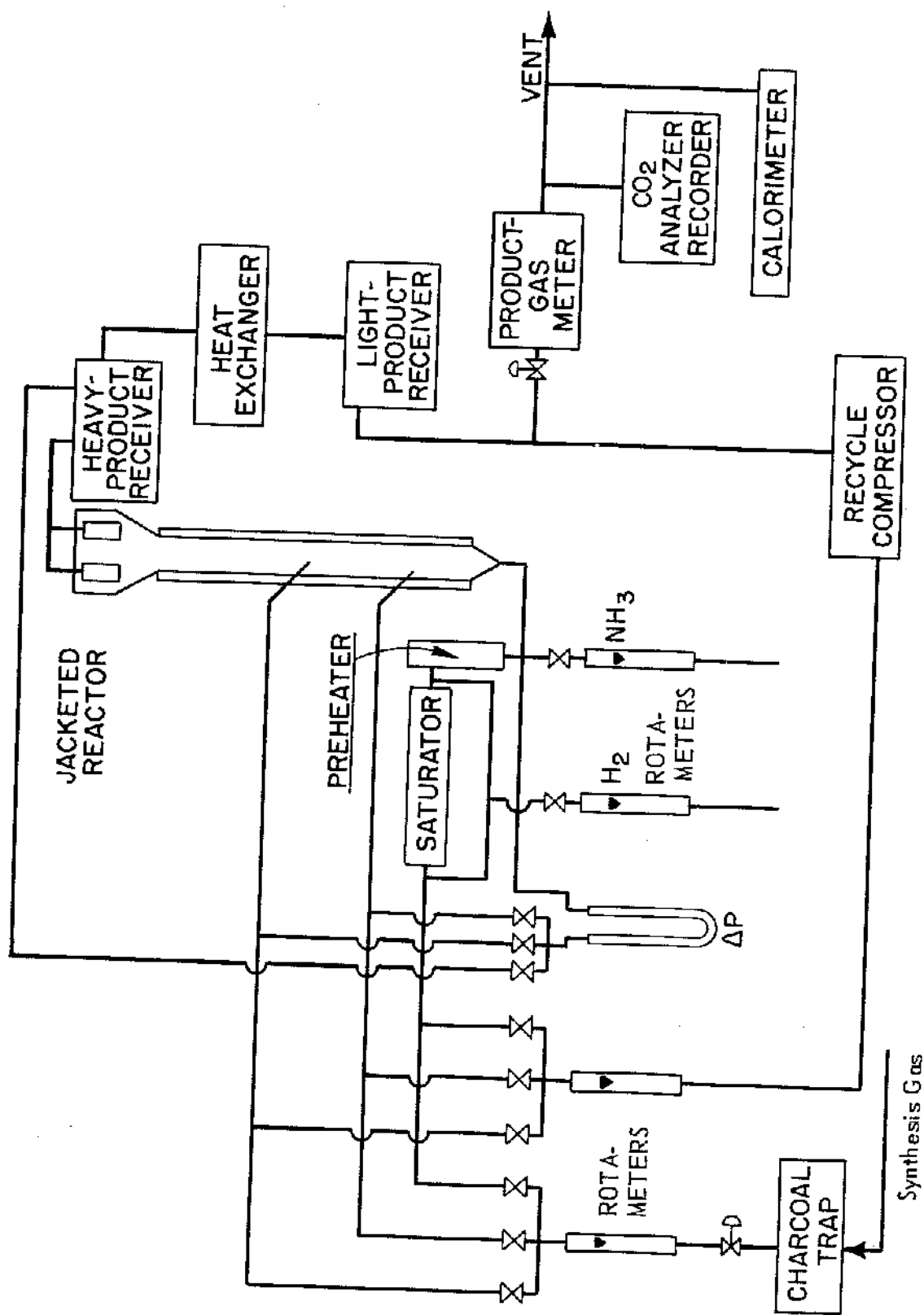


Figure 24. - Multiple-feed, fluidized-catalyst reactor flow diagram.

throttle valves control the flow of the recycle-gas streams, which join the synthesis-gas lines just before the synthesis gas is preheated. A differential manometer is arranged so that pressure drops between a point just before the electrical preheater and any or all the gas-entry points may be measured. Figures 25 and 26 show the control panel of the unit and the method of introducing the two upper feed-gas streams into the reactor.

Temperatures of points within the bed at heights of 1, 10, 20, 38, and 60 inches above the reactor bottom are measured by iron-constantan thermocouples located inside the baffle tube. In addition to these temperatures, seven additional thermocouples measure the temperatures of the internal and external walls of the electrical preheater, the liquid and vapor zones and external wall of the heat-exchanger jacket, and the temperature of each filter. Temperatures are recorded on a recording-indicating potentiometer. The reactor body and the flange sections of the unit are heated in a manner identical to that in the conventional unit. The flange heater coil may be seen at the bottom of the unit in figure 26.

The operating limits of this unit are approximately 480° C. and 300 p.s.i.g. At these operating conditions, based upon a maximum gas velocity for fluidization of 2 ft. per sec., a total flow of fresh-feed and recycle gas of approximately 320 std. c.f. per hr., and a recycle ratio of approximately 3:1 can be obtained. The reactor holds approximately 350-500 cc. of catalyst finer than 80-mesh, which yields a settled-bed height of 3-4 feet.

Operating Procedures

All of the catalysts tested in this unit contained nickel. After the catalysts were preheated and in place in the reactor, the temperature of the reactor was reduced to 300° C., the pressure was increased to 300 p.s.i.g., and, with hydrogen in the system, recycle gas was admitted into the bottom feed point of the unit at a rate sufficient to assure complete fluidization of the bed (linear gas velocity > 0.5 ft. per sec.). Small quantities of recycle gas were admitted into each of the upper feed lines to prevent catalyst from being blown up into the tube openings. After adjusting the recycle flow rates, synthesis gas was slowly admitted into the bottom feed point until an increase in temperature at the 1- and 10-inch thermocouple positions was observed. Synthesis gas was then admitted into the 2 upper feed points at a rate to give a minimum temperature difference among the 5 thermocouples in the catalyst bed. This stepwise increase of synthesis-gas flow was continued until the desired fresh-feed space velocity was obtained. Recycle gas was added at each of the feed gas points during and after the synthesis-gas flow adjustments to reduce the observed temperatures within the catalyst bed.

During the period in which the activity of the catalyst was high and stable, reaction temperatures were controlled by the redistribution of gas flow, the use of recycle gas, and the control of nitrogen pressure in the Dowtherm jacket. As soon as the activity of the catalyst began to decrease, synthesis-gas flow rates had to be reduced and recycle ratios increased to maintain controllable temperatures within the bed. Normally, a fresh-feed space velocity of approximately $7,100$ hr.⁻¹ and a recycle ratio of about 1:1 were used in the tests. If, however, a temperature difference of more than about 10° - 15° C. was observed between any of the thermocouples in the catalyst bed, attempts were made to reduce the differences by readjusting the various gas flows to the reactor. A test was continued until the carbon dioxide- and water-free contraction decreased below 69 percent, a conversion that corresponded to a 900 B.t.u. fuel gas.

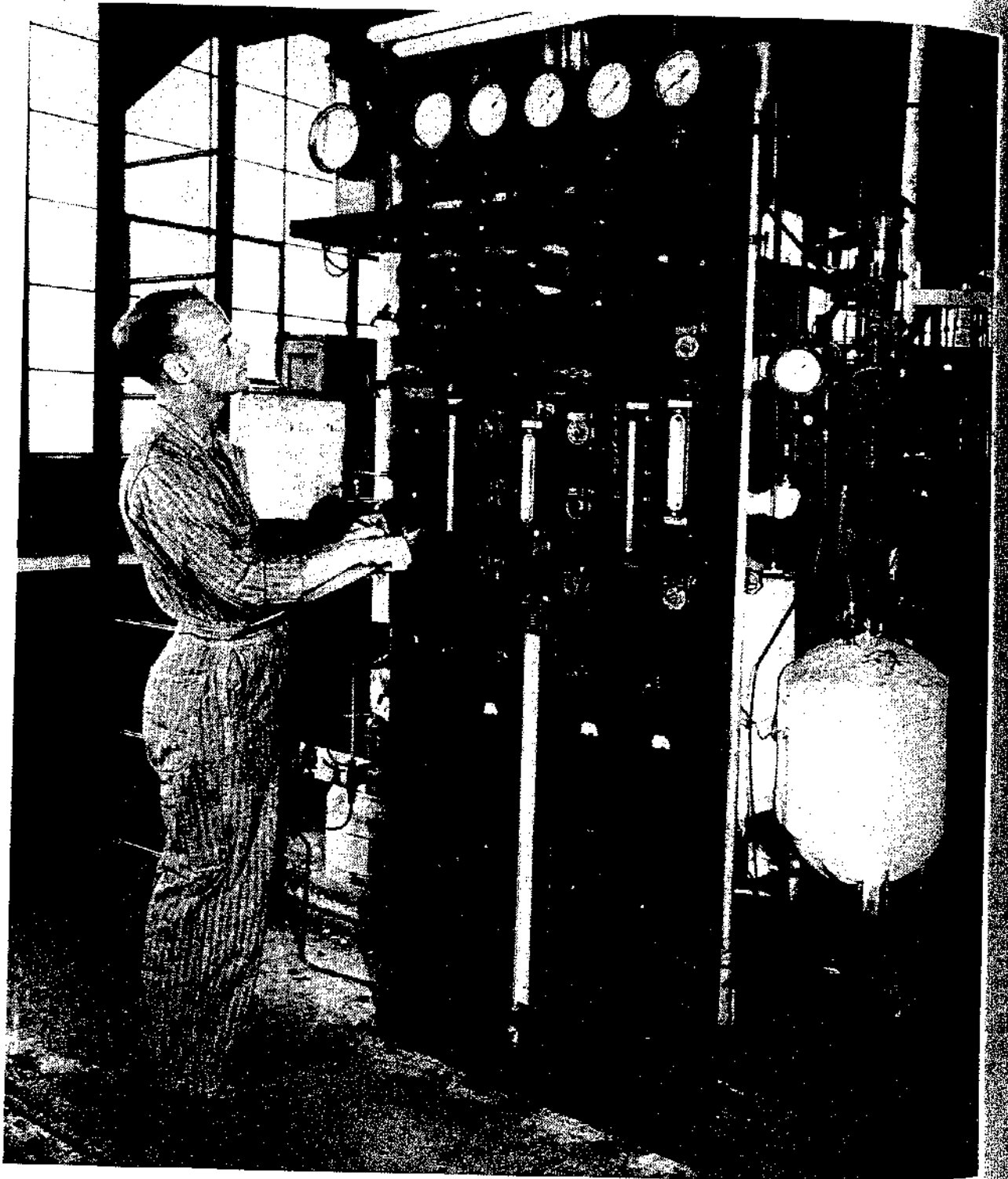


Figure 25. - Control panel, multiple-feed unit.

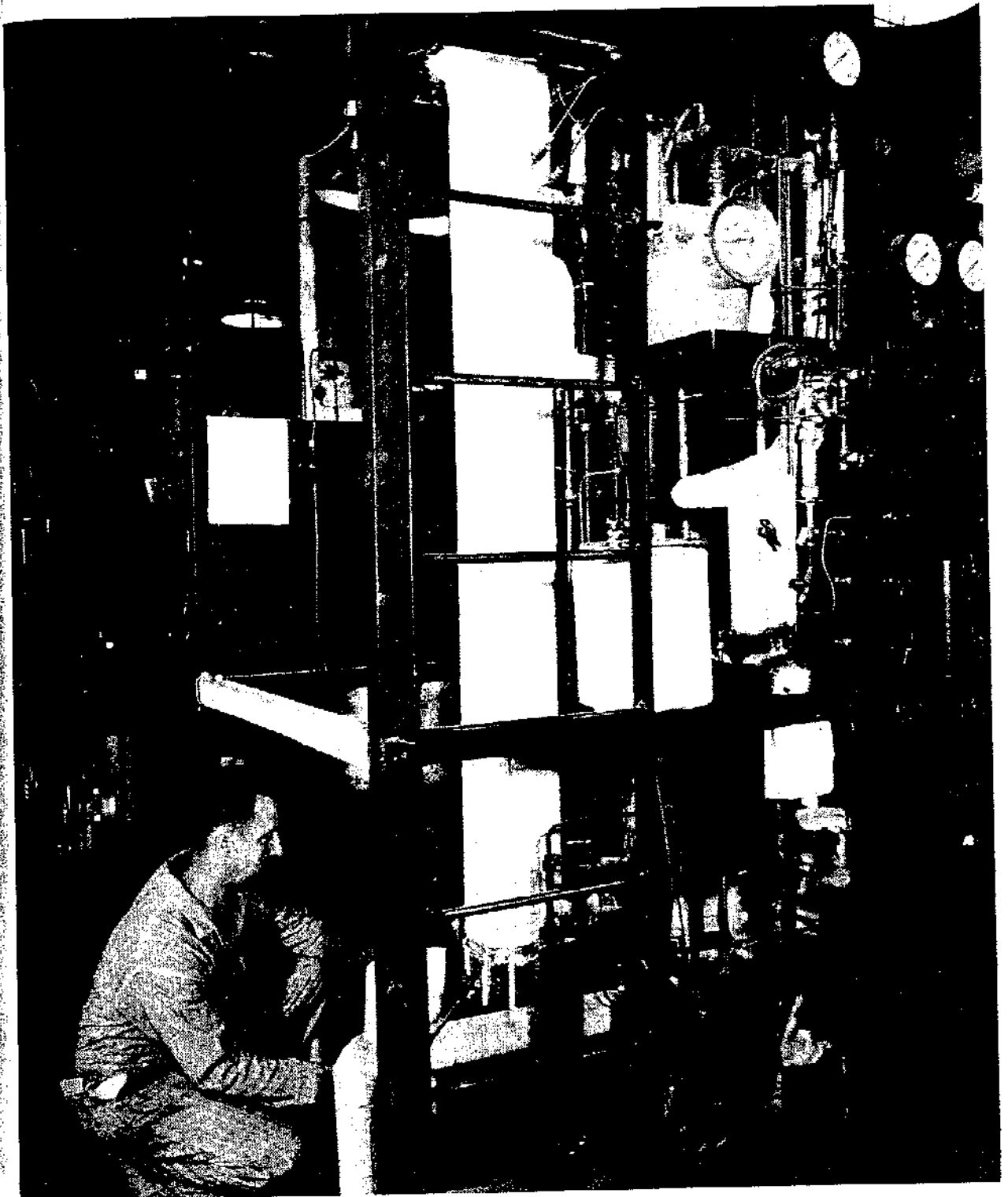


Figure 26. - Side view, multiple-feed unit.

Results of Nickel-Catalyst Tests in Multiple-Feed Bed

Catalyst L-6025 was the first material tested in the multiple-feed unit. Temperature differences of less than 10°-15° C. were easily maintained during normal operation at space velocities of over 7,100 hr.⁻¹, and at recycle ratios of less than 1:1. These low gradients were in direct contrast to those obtained in the conventional bed with the same catalyst. As the catalyst activity decreased, however, increased difficulty was encountered in controlling the catalyst-bed temperatures. Initially, a temperature decrease was observed at the 1- and 10-inch thermocouple positions, and a temperature increase was observed in the upper sections of the catalyst bed and in the filters. This condition continued to become more severe, despite readjustment of the inlet-gas distribution, and the test was terminated after approximately 145 hours. A 69-percent or better carbon dioxide-free contraction was maintained for about 45 hours of the test period.

Attempts were made to increase the process life of this catalyst by modifying the composition of the material. Table 6 is a summary of the results of tests made with the modified catalysts. In almost every instance, the methane yields were high enough to give a gas having a heating value of over 900 B.t.u. per cu. ft. at calorific efficiencies approaching 100 percent. A typical product-gas analysis for one of the tests is given in table 7.

During these tests it was observed that the catalysts suffered a decrease in bulk volume and particle size. Table 8 shows the physical changes occurring in some of the catalysts that were tested.

In order to determine at what stage of the process these changes occurred and the effect that these changes had on catalyst activity, batches of catalysts L-6036 and L-6046 were reduced in the usual way and were discharged from the reactor when reduction was completed. By this technique, it was possible to study the changes in particle characteristics after each phase of the operation. During reduction both catalysts decreased in bulk volume by about 30 percent and the percentage of catalyst fines increased about 10 percent. Catalyst L-6036 was tested in the fluidized unit under normal synthesis conditions after all the material finer than 200-mesh was separated from the catalyst charge. The synthesis process resulted in an additional 20-percent reduction in catalyst volume and a 36-percent increase in catalyst fines. Catalyst L-6046, however, which was tested with all the material finer than 140-mesh removed from the catalyst, suffered only a 5-percent reduction in volume and a 7.6-percent increase in catalyst fines during synthesis. The activity of both catalysts was not appreciably affected by removing the catalyst fines, but the process life of both materials was definitely shortened.

During the time that synthesis gas with a hydrogen-carbon monoxide ratio of 2.5 was being used, it was observed that very small quantities of carbon were being deposited on the catalyst during synthesis. The synthesis gas ratio was increased to 3.0 in an attempt to prevent the small amount of carbon deposition and any catalyst spalling owing to this deposition. The results of this change in synthesis-gas ratio, however, were inconclusive.

TABLE 6. - Fluidized-bed catalyst evaluation

Theoretical catalyst composition ^{1/}	Catalyst number	Fe ₂ O ₃	Average temperature	Fresh feed, SVH	Recycle ratio	Life, 2/ hours	Process life, lbs. CH ₄ /lb. M
NiO-100 (21.2%), Al ₂ O ₃ 159, kaolin 97	L-6025	2.5	350	7,400	1:1	45	-
NiO-100 (24.1%), MgO 125, kaolin 97	L-6034	2.5		temperatures uncontrolable			-
NiO-100 (35.6%), Al ₂ O ₃ 7.3, MnO 25.6, kaolin 97	L-6036	2.5	330	2,800-10,000	0.8:1-1.3:1	220	-
NiO-100 (40.3%), Al ₂ O ₃ 7.3, MnO 25.6, kaolin 97	L-6036.1	2.5	350	7,500	1:1	150	750
NiO-100 (36.8%), Al ₂ O ₃ 7.3, MnO 25.6, kaolin 97	L-6036.2	3.0	343	7,500	1.5:1	132	1,200
KiO-100 (17.8%), Al ₂ O ₃ 34.4	L-6037	2.5	365	900	2.5:1	Inefficient activity.	
NiO-100 (35.1%), Al ₂ O ₃ 7.3, MnO 25.6, activated alumina 75 ..	L-6039	2.5	360	7,500	1:1	174	900
NiO-100 (18.2%), Al ₂ O ₃ 7.3, MnO 25.6, activated alumina 75 ..	L-6039.1	3.0	340	3,600	1:1	78	-
NiO-100 (7.2%), Mn 43, activated alumina 142	L-6042	2.5	345	7,500	0.8:1	6	-
NiO-100 (26.0%), Al ₂ O ₃ 7.3, MnO 25.6, cracking catalyst 135 ..	L-6043	2.5	345	7,000	1:1	60	-
NiO-100 (6.6%), Al ₂ O ₃ 52, Norton SA 103 pellets - crushed 910	L-6044	2.5	400	5,000	1:1	Inefficient activity.	
NiO-100 (19.0%), Al ₂ O ₃ 7.3, MnO 25.6, silica 321	L-6045	2.5	350	7,000	0.4:1	14	-
NiO-100 (15%), Al ₂ O ₃ 7.3, MnO 25.6, activated alumina 240 ..	L-6046	2.5	380	7,500	1:1	8	-
NiO-100 (20.5%), Al ₂ O ₃ 5.3, MnO 19.2, activated alumina 193 ..	L-6047	2.5	425	3,000	1.5:1-2.5:1	54	-
NiO-100 (27.2%), Al ₂ O ₃ 7.3, MnO 25.6, Filarsol 8-185	L-6051	3.0	350	7,500	0.7:1	237	2,500
NiO-100 (17.3%), Al ₂ O ₃ 7.3, MnO 21.0, activated alumina 240 ..	L-6053	3.0	362	7,000	1:1	550	6,500
NiO-100 (42.4%), MnO 13.6, Kieselsghur 78.4	L-6057	3.0	370	7,000	1:1	380	4,000
NiO-100 (6.4%), magnetite 147C	L-6055	2.5	370	3,400-1,500	1:1	-	-
Co-100, Al 99	L-6049	3.0	321	14,000	2:1	1	-

^{1/} Based upon ingredients. () Percentages of NiO determined analytically. ^{2/} Above 60% CO₂-free contraction.

NOTE: All catalysts except L-6049 were reduced at 350-400° C. 100 p.s.i.g. (All runs at 300 p.s.i.g.).

All Catalysts were prepared by precipitating nitrate salts on various supports with K₂CO₃ except the following:

- L-6037 - Mn and Al nitrates were precipitated without a support.
- L-6042 and L-6047 - Supports impregnated with nitrate salts which were later precipitated with K₂CO₃.
- L-6035 - Magnetite impregnated with Ni(NO₃)₂·6H₂O.
- L-6049 - Raney cobalt 1 1/2 Al extracted with KOH solution.

TABLE 7. - Product gas analysis, catalyst L-6051

Catalyst composition: NiO-Al ₂ O ₃ - MnO ₂ -Filtrol S, 100:7.3:25.6:18.5	
Average reactor temperature	°C. 350
Reactor pressure	p.s.i.g. 300
Fresh-feed space velocity, hr. ⁻¹	7,500
Recycle ratio	0.7:1
H ₂ /CO ratio	3.0
Time of sample after initiation of synthesis	hours 33
C ₁	percent 82.2
CO ₂	do. 3.54
H ₂	do. 13.3
CO	do. 0.95
Conversion H ₂ +CO	do. 95.8
Usage ratio (H ₂ /CO)	2.97
Gross heating value	B.t.u. per cu. ft. (CO ₂ , H ₂ O free) 963
Calorific efficiency	percent 94.7

TABLE 8. - Catalyst changes during processing

Catalyst No.	L-6036	L-6037	L-6039	L-6042	L-6043
Initial vol. cc.	400	310	400	450	450
Initial wt. gm.	304	210	356	416	192
Percent wt. loss on reduction (calculated) ..	28.0	5.00	24.4	5.50	16.0
Percent wt. loss, discharged catalyst	37.0	12.0	35.5	7.70	18.0
Percent vol. loss, discharged catalyst	44.0	-	45.0	6.00	40.0
Weight percent increase over initial unre- duced charge, particles 200-mesh	9.30	3.10	11.0	2.00	5.00
Catalyst No.	L-6045	L-6047	L-6051	L-6053	L-6057
Initial vol. cc.	425	450	400	450	450
Initial wt. gm.	288	303	222	323	281
Percent wt. loss on reduction (calculated) ..	11.0	10.6	18.0	13.0	9.00
Percent wt. loss, discharged catalyst	26.0	9.00	20.3	13.7	17.0
Percent vol. loss, discharged catalyst	50.0	24.5	25.0	35.0	35.0
Weight percent increase over initial unre- duced charge, particles 200-mesh	34.0	17.8	3.20	13.7	20.3

The first thorium-promoted catalyst, L-6053, ran for 550 hours to yield a process life of 6,500 lb. CH₄ per lb. Ni. A second thorium-promoted material, L-6057, which was initially formulated by the Gas Research Board,^{26/} ran for 380 hours to yield approximately 4,000 lb. CH₄ per lb. Ni. However, two attempts at reproducing the results obtained from catalyst L-6053 with other batches of this same catalyst were unsuccessful. The only difference between the initial batch of this catalyst and the two unsuccessful batches of material was a color difference that could only be attributed to the temperature at which the various batches of material had been dried after washing. The initial catalyst had been dried at approximately 180° C., and the 2 later batches at approximately 120° C. Believing that the higher drying temperature was desirable, a charge of raw catalyst remaining from one of the unsuccessful runs was redried at 180° C. and tested under synthesis conditions. The additional drying temperature increased the life from 150 to 185 hours. It was believed that the double-drying technique used with this catalyst might have affected the activity of the material, and another batch was prepared and dried at 180° C. This batch of catalyst ran for 425 hours and yielded approximately 5,500 lb. CH₄ per lb. Ni. An additional test was made with a fourth batch

^{26/} See work cited in footnote 10.

of material, and the catalyst ran for 336 hours producing approximately 3,700 lb. CH₄ per lb. Ni. Additional tests were made with catalysts dried at various temperatures, and the results of this series of tests are summarized in table 9.

In every test made with nickel catalysts in both fluidized units, examination of the thermocouple well revealed a slow but definite deposition of metallic nickel on the tube wall. No detailed attempt was made to investigate or explain this phenomenon.

TABLE 9. - Thorium-promoted nickel-alumina catalysts

Catalyst number	Drying temp., °C.	Catalyst density, gm./cc.	Initial activity temp., °C.	Operating temp. range, °C.	Life, hr.	Approximate yield, lb. CH ₄ / lb. Ni
L-6053.1	120	.72	351	350-374	28	330
L-6053.2	120	.70	345	350	150	2,200
L-6053.21	120 (redried at 180)	.70	364	355-370	185	2,700
L-6053.8	150	.74	369	363-372	82	970
L-6053.10	170	.70	363	360-372	156	1,800
L-6053	180	.73	370	360-377	550	6,500
L-6053.3	180	.81	374	361	425	5,500
L-6053.4	180	.74	360	365	336	3,700
L-6053.7	180	.74	373	370-375	406	4,800
L-6053.9	190	.78	365	363-372	110	1,300
L-6053.5	210	.74	380	373-380	112	1,300
L-6053.6	222	.76	377	375-380	256	3,000
L-6053.11	250	.68	380	364-375	207	2,400

Discussion of Nickel-Catalyst Tests in Multiple-Feed Bed

The operation of small-diameter fluidized-reaction equipment appears to be affected by the slow loss of catalyst activity with time, by the spalling of catalyst particles during reduction and synthesis, and by an apparent lack of circulation of particles between various zones of the bed. No one of these phenomena could create operating difficulties in a fluidized bed if it occurred in the absence of the others; however, when all three occur simultaneously, the operation of the unit becomes extremely difficult. If, as the data indicate, the coarser particles of catalyst have a shorter process life than the finer, and if, as some investigators believe,^{27/} there is a segregation of particles in a fluidized column, the initial spalling of particles during reduction can lead to operating difficulties. These difficulties might be partly solved in larger-size equipment, in which better mixing might be achieved. The most practical solution, however, would be to develop catalysts with longer process lives that did not break up during reduction and synthesis.

The overall advantages of using fluidized-bed and gas-distribution techniques are clearly shown by a comparison of the data obtained when using catalyst L-6057 in this type of equipment with the results obtained by the Gas Research Board using this same catalyst in bench-scale, fixed-bed equipment. The 30-percent increase in methane yield obtained by this laboratory while producing gases with heating values of over 900 B.t.u. per cu. ft., as compared with the British yield while producing 400-600 B.t.u. gas, is an indication of the value of good temperature control of the reaction equipment.

^{27/} Matheson, G. L., Evaluation of Finely Divided Solids: United States Patent 2,683,685, July 1954.

The factors that contribute to the process life of a catalyst are not as clearly defined as was thought when the thorium-promoted materials were first tested. Although it was originally believed that the use of thorium as a promotor was responsible for the increased process life of the catalysts, the experience with the catalyst-preparation techniques suggests that conclusions in this respect would be premature without a thorough investigation of the effects of catalyst preparation on process life. It is conceivable that some of the original materials, if prepared under slightly different conditions, might yield excellent process lives.

The degree of purity of the synthesis gas required for a successful methanation process utilizing nickel catalysts is still subject to a great deal of question. Wainwright, Egleson, and Brock have shown that a sulfur content of 0.4 grains per M c.f. in the synthesis gas results in a process life of approximately 1,000 lb. CH₄ per lb. Ni (based on the nickel content of the materials used in preparing the catalyst) with a catalyst similar in formulation to catalyst L-6036.^{28/} These results along with the experience of this laboratory with the activated charcoal traps seem to indicate that the maximum allowable sulfur limits of a synthesis gas that is to be utilized for methanation over nickel catalysts are quite low. More detailed investigations must be conducted, however, before any definite conclusions can be reached.

CONCLUSIONS

Although the work described in this report was limited to relatively small-scale studies, it can be generally concluded that, with nickel catalysts, high rates of fuel-gas production can be obtained only if the heat liberated during the reactions is distributed over the whole catalyst bed. The heat may be distributed by using the multiple-feed designs previously discussed; however, the success of this type of heat-distributing technique in equipment larger than the 1-inch diameter bed studied is something that must be determined by actual pilot-plant investigations.

It was also established that nickel is superior to iron as a methanation catalyst if the process is considered in terms of an operation producing only high heating-value fuel gas. In a combined operation producing both gaseous and liquid products, however, iron might prove to be a more suitable catalytic material.

The techniques of catalyst preparation appear to be major factors in determining the process lives of nickel catalysts. The actual effects of the various preparation steps are not completely understood, and further investigations into this phase of the problem must be made.

Sulfur is extremely detrimental to the activity of nickel catalysts. Although it is clear that the sulfur content of the synthesis gas that is used must be very low, not enough data exist for determining the maximum allowable sulfur concentrations that can be used with a nickel catalyst in commercial operations.

^{28/} Wainwright, H. W., Egleson, G. C., and Brock, C. M., Laboratory-Scale Investigation of Catalytic Conversion of Synthesis Gas to Methane: Bureau of Mines Rept. of Investigations 5046, 1954, 10 pp.