EXPERIMENTAL PROGRAM

The experimental program that was undertaken by the Bureau of Mines had two long-term objectives: (1) Development of a process capable of producing fuel gases with heating values of over 900 B.t.u. per cu. ft. that could be utilized in commercial-size installations; and (2) development of catalysts that would have process lives of such length that the contribution of the catalyst cost to the total cost of the process would be small.

The major difficulties that one may encounter in a methanation process, together with the schemes proposed in this investigation by the Bureau of Mines for the solution of these difficulties, are as follows:

1. The reactions associated with the production of methane from synthesis gas are extremely exothermic, and failure to provide an adequate heat-removal system for the process equipment can result in premature catalyst failure, unfavorable equilibrium conditions for the production of methane, and, in extreme situations, damage to process equipment.

To avoid this difficulty fluidized-bed equipment was selected to carry out the bench-scale phase of this work. It was believed that the excellent heat-transfer characteristics of fluidized systems under conditions of high feed-gas throughputs and the fact that fluidized systems can be operated on a continuous basis with respect to catalyst replacement indicate that this type of equipment would be well suited for the methanation process.

2. Using synthesis gases having hydrogen-carbon monoxide ratios of less than about 2.7 generally results in carbon deposition in the temperature and pressure ranges that yield the highest concentrations of methane. Failure to prevent carbon deposition can result in poor process efficiency, excessive catalyst cost, and excessive equipment maintenance time.

If a synthesis gas having a hydrogen-carbon monoxide ratio of approximately 1 is produced in the gasification step, the theoretical yield of carbon dioxide produced from this gas in the methanation step would be the same as would be produced if this gas was shifted by reaction (2) to a hydrogen-carbon monoxide ratio of approximately 3 and then catalytically converted to methane. Since the carbon dioxide-scrubbing costs would be about the same for both cases, the only additional cost would be that due to the shifting step, and this cost would be small in comparison to the cost problems of carbon deposition that would be present if the ratio of the synthesis gas was not shifted. Accordingly, the Bureau of Mines based the work on the assumption that the ratio of the synthesis gas could be varied if the experimental conditions indicated that such a change was desirable.

3. Catalysts that are generally employed to convert synthesis gas to methane are extremely susceptible to the poisoning effects of impurities such as sulfur compounds. These impurities can result in excessive catalyst costs for the process.

In most localities the maximum inorganic sulfur limits of a distributed fuel gas are set by local ordinances or legislation. These limits are about the same as would be found in a fuel gas that is manufactured from a synthesis gas pure enough to be used for Fischer-Tropsch synthesis. Because of this fact, it is reasonable to expect that an industrial process would utilize essentially sulfur-free synthesis gas (<1 grain per M c.f.). Accordingly, it was planned that all of the synthesis gas used in this work would be purified to less than 1 grain sulfur per M c.f.

Experimental Procedures

The experimental program was divided into two phases: Small-scale fixed-bed and bench-scale fluidized-bed testing. Catalysts were, in most instances, tested for methanation activity in small laboratory-scale fixed-bed testing units, which are identical with those used in Fischer-Tropsch catalyst-development work.[21] The utilization of these small units served as a screening process and permitted determination of methanation activity of various materials in much less time and at less expense than would have been required in larger scale equipment. Heat-transfer difficulties were avoided in these units by operating them at low space velocities. If the tests in the fixed-bed equipment revealed that the material was an active methanation catalyst, a study of this material was scheduled for the larger bench-scale fluidized unit.

Criteria of Catalyst and Process Evaluation

Three criteria were used to evaluate catalysts and process design. The first criterion was the heating value of the product gases, referred to 0° C. and a pressure of 1 atmosphere and corrected to a carbon dioxide- and higher hydrocarbon-free basis. The higher molecular weight hydrocarbons containing more than three carbon atoms were eliminated from the calculations of heating value of the product gas because these materials tend to condense in high-pressure pipelines and it was believed that a normal process would require that these materials be removed from the gas before it was compressed for pipeline distribution.

The second criterion that was used was the calorific-conversion efficiency, which hereafter will be referred to in this manuscript as calorific efficiency, and which is defined by the equation

$$CE(\%) = 100 \; \frac{\sum_{i=1}^{i=3} C_i X_i + \sum_{j=2}^{j=3} C_j X_j}{A C_1 X_k}, \tag{7}$$

where X_i and X_j are the yields, in volume units at normal reference conditions, per unit time of the C_1 to C_3 paraffin and C_2 and C_3 olefin hydrocarbons, respectively; X_k is the feed rate of synthesis gas, in volumes per unit time; C_i and C_j are the gross heating values of components i and j, respectively, in B.t.u. per unit volume at normal reference conditions; C_1 is the gross heating value of methane; and A is the stoichiometric yield of methane according to reaction (1), in volumes per unit volume of synthesis gas. This equation takes into consideration only that portion of the synthesis gas that is converted into an acceptable fuel gas, and the value obtained from the equation is the part, expressed as percent, of the maximum possible theoretical heating value that can be obtained from a synthesis gas having a specific hydrogen-carbon monoxide ratio. As an example, a synthesis gas having a hydrogen-carbon monoxide ratio of 3:1 and producing only methane would yield a calorific efficiency equal to 100 percent.

21/ Storch, H. H., Golumbic N., and Anderson, R. B., The Fischer-Tropsch and Related Synthesis: John Wiley & Son, New York, 1951, p. 152.

In the later stages of the work when high-activity nickel catalysts were being tested, it was found that these two criteria were insufficient to evaluate the catalysts and a third criterion, the process life of the catalyst, was established. This value was used to evaluate nickel catalysts only and is expressed as total yield of methane in pounds per pound of nickel in the catalyst.

Synthesis Gas

The synthesis gas that was used in both the fixed- and fluidized-bed testing was manufactured in a Girdler-type synthesis-gas plant from natural gas and steam. After manufacture, the synthesis gas was stored in a wet gas holder until used. For fixed-bed work, the gas was compressed to about 2,100 p.s.i.g., passed through an activated-charcoal trap, and charged into standard gas cylinders. For the fluidized-bed work, the gas was compressed to 400-600 p.s.i.g., purified by passing through an activated charcoal trap, and then passed directly to high-pressure manifolds that carried it to the reaction equipment. The sulfur content of both the 2,100-p.s.i.g. gas and the 400- to 600-p.s.i.g. gas was approximately 0.1 grain per M c.f. after leaving the charcoal trap. Synthesis gases with hydrogen-carbon monoxide ratios of 1, 2, 2.5, and 3 were prepared for this work.

Gas Analyses

Both synthesis gas and product gas were analyzed in a Consolidated Engineering Mass Spectrometer. During operation carbon dioxide concentrations in the product gas were determined in a conventional Haldane apparatus.

Catalysts: Preparation and Pretreatment

Although some naturally occurring and some commercially manufactured materials were tested, most of the catalysts used in both the fixed- and fluidized-bed tests were prepared in the laboratory. These materials were, with some exception, of the supported-metal type and were prepared by either impregnation or precipitation techniques. In order to impregnate a support, a solution of the nitrate salts of the metal and promotors was added to a quantity of support to form a slurry. The slurry was then evaporated to dryness over a steam bath, and the dried residue was placed in an oven, which was maintained at approximately 600° C. to convert the nitrate salts to oxides. If a precipitated material was desired, the slurry of nitrate salts and support was treated with a solution of potassium carbonate. The treated slurry was then heated to the boiling point with constant stirring and filtered. The filtered solid material was washed with hot water and was then dried in a drying oven for approximately 16 hours. The dried residue obtained from either technique was crushed to 6- to 8-mesh (U.S.S.) for fixed-bed testing or a size smaller than 80-mesh for fluidized-bed testing.

One group of catalysts composed of magnetite and ball clay was prepared by firing a dried mixture of magnetite and ball clay in a furnace at approximately 600° C. The sintered material was then crushed to the desired sieve size for testing.

Catalysts were pretreated in a number of ways, although in a few instances no pretreating was done. In the latter case, the catalyst was charged to a particular unit immediately after sieving and synthesis was initiated with the raw catalyst. In most cases, however, the catalyst was reduced with hydrogen before synthesis, and, in the case of iron catalysts, most of the materials were also subsequently nitrided with anhydrous ammonia before the initiation of synthesis.

For the fixed-bed work, the reduction was carried out in a special reduction unit at 350°-400° C. and atmospheric pressure for approximately 8 hours, unless the material was to be nitrided, in which case the reduction was continued until an X-ray analysis of the catalyst revealed that at least 90 percent of the iron was present as →-iron. Nitriding was carried out in this same unit by passing anhydrous ammonia over the catalyst at 350° C. and atmospheric pressure until X-ray analysis showed that an →-phase nitride, Fe_2N, was obtained. This nitride corresponds to a nitrogen content in the weight range of 7 to 11 percent and an atom ratio of nitrogen to iron in the range 0.314 to 0.498.

In the case of the fluidized-bed work, both the reduction and nitriding of the catalyst were carried out in the reactor itself.

Certain nickel catalysts that were reduced in the fluidized bed were discharged and examined after reduction was complete, and then were recharged into the fluidized reactor. This technique was used to permit determination of the effects of reduction on the size consist and bulk density of the catalyst. In the fluidized units, the reduction of nickel catalysts was continued until the formation of water had almost ceased, a procedure that required from 3 to 72 hours, depending upon the type of catalyst being reduced.

Before synthesis the Raney-cobalt and Raney-nickel alloys that were tested were either oxidized with steam followed by reduction with hydrogen or treated with a solution of either sodium or potassium hydroxide to remove part of the aluminum from the alloy. The extracted catalysts were charged to the reactor in a wet condition but were dried in a hot stream of helium or hydrogen before synthesis was initiated.

FIXED-BED TESTING

Equipment Description

The fixed-bed reactor is shown schematically in figure 13. The reactor consists of a 1/2-inch, Schedule 40, steel pipe 12 inches in length surrounded by an electrically heated Dowtherm heat-exchanger jacket. The reactor tube, which holds about 55 cc. of catalyst, contains a 1/4-inch steel thermocouple well. A second thermocouple well is inserted down through the top of the heat-exchanger jacket. Temperatures in the bed and in the jacketed section of the reactor are measured by chromel-alumel thermocouples and are recorded on an indicating-recording potentiometer. Jacket temperatures are maintained by controlling nitrogen pressure over boiling Dowtherm in the jacket using a mercury manostat. The operating limits of the unit are approximately 300 p.s.i.g. at 400° C.

A flow diagram for the fixed-bed apparatus is shown in figure 14. Synthesis gas of any desired hydrogen-carbon monoxide ratio is fed to the reactor from standard gas cylinders through an activated charcoal trap, macrothrottle and microthrottle valve, and a flow meter. The synthesis gas enters the reactor through the top and flows down through the catalyst bed. The product gases leave the reactor and pass through a trap system to recover liquid and solid products, and then through a pressure regulator, carbon dioxide-scrubbing system, sight-bubbler, product-gas meter, and out to atmosphere. Provisions are made for sampling the product gas both ahead of and after the carbon dioxide scrubber; however, in normal operation, only the latter sampling point is used.
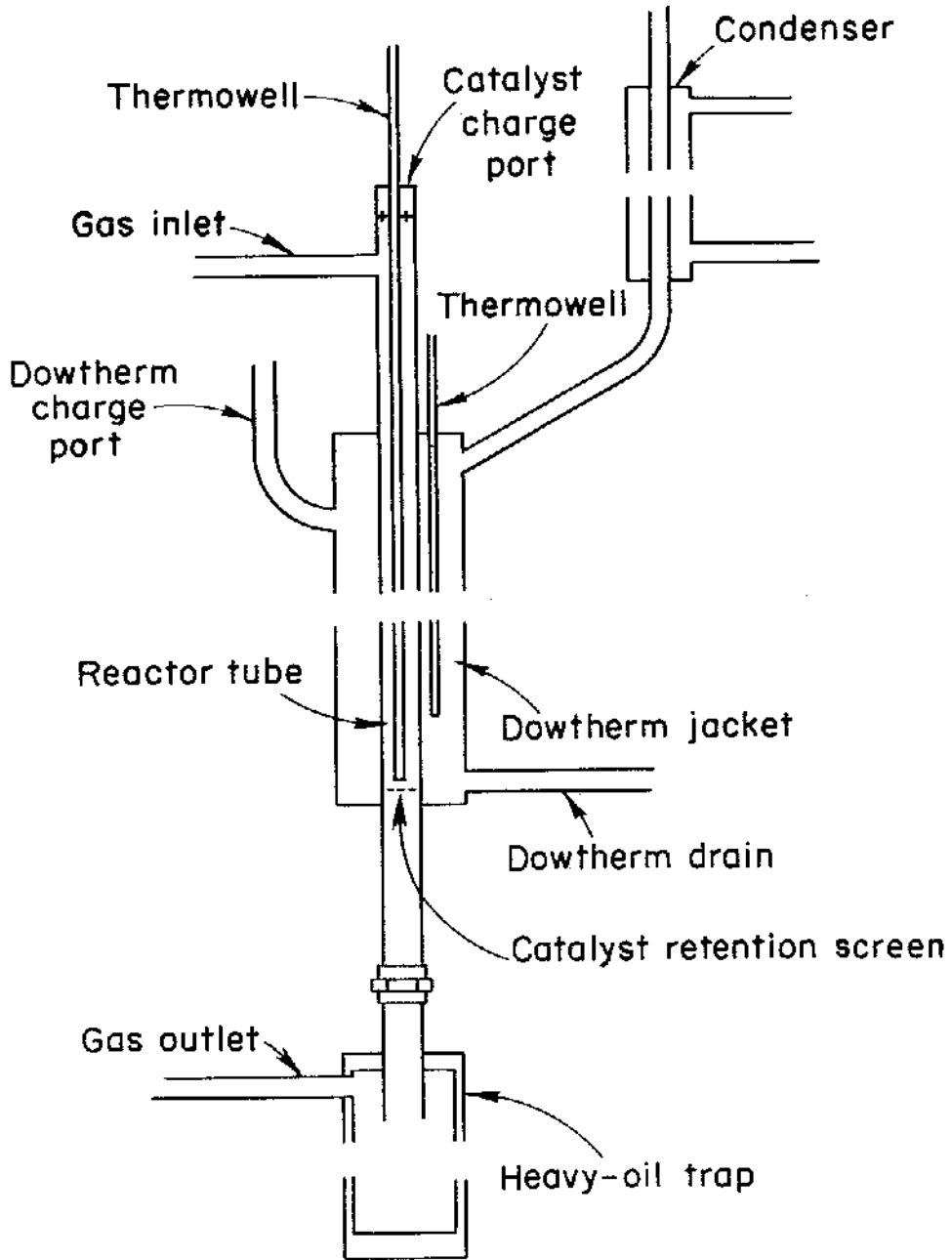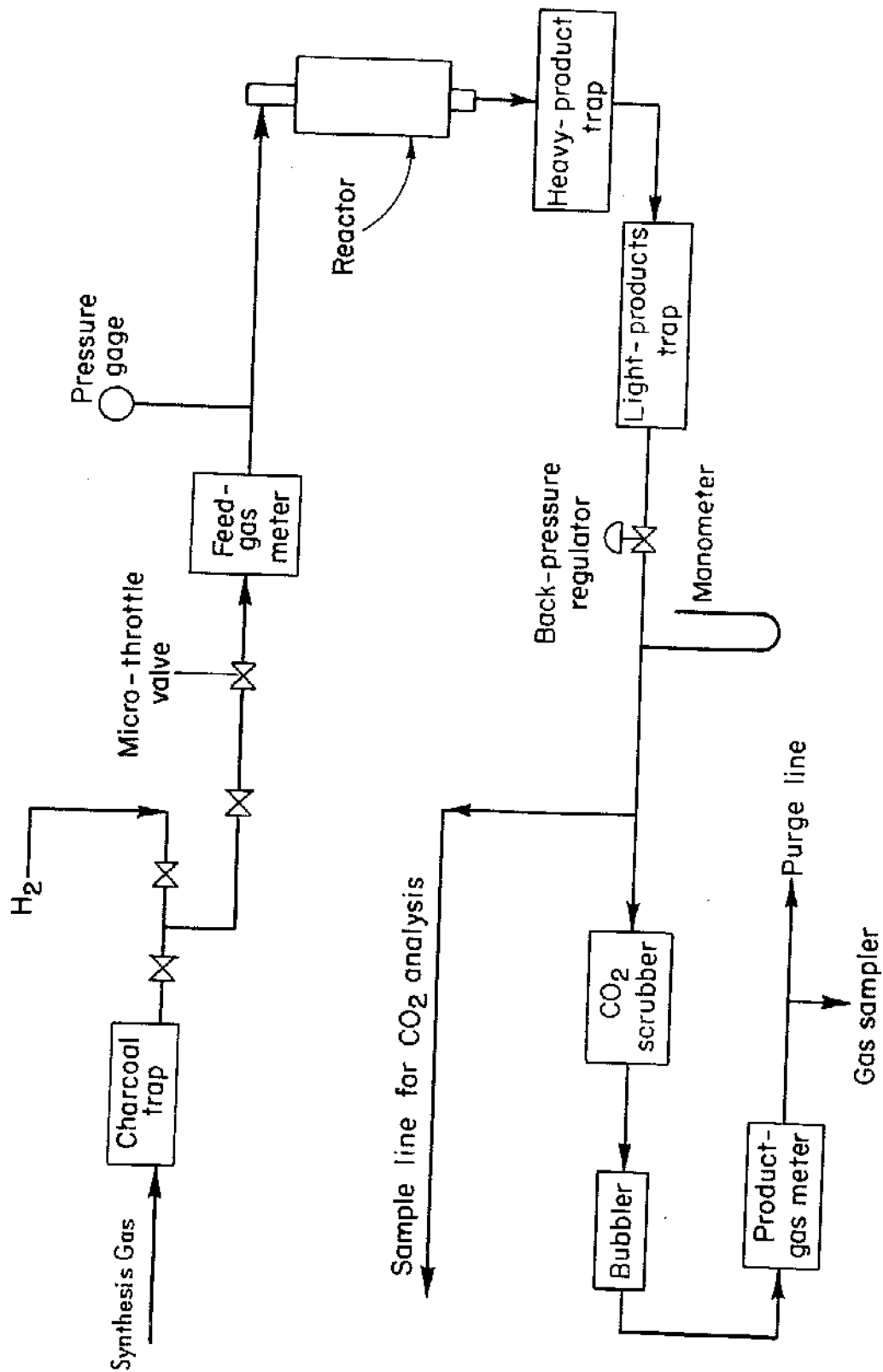
Figure 13. - Fixed-bed catalyst reactor.

Figure 14. - Flow diagram of fixed-bed-catalyst testing apparatus.

Operating Procedures

Synthesis gas was admitted to the reactors at space velocities ranging from 100 to 300 hr.[122]/ and at pressures ranging from 0 to 300 p.s.i.g. In some instances, space velocities were increased to as high as 3,000 hr.$^{-1}$ after the initiation of synthesis; however, in normal operation 300 hr.$^{-1}$ was rarely exceeded.

Results

The results of the fixed-bed testing are summarized in table 1. Iron catalysts were less active than nickel catalysts, and impregnated nickel catalysts were less active than precipitated nickel catalysts. Little difference in activity was observed between precipitated nickel catalysts and extracted Raney alloys. Oxidized and reduced Raney alloys were inactive for the production of methane.

In general, iron catalysts produced large quantities of C_3 + hydrocarbons (those having more than 3 carbon atoms), and it was difficult to obtain product gases with heating values over 800 B.t.u. per cu. ft. When such heating values were obtained, the calorific efficiencies for the process were usually quite low because of the excessive yields of high molecular-weight hydrocarbons and carbon. In contrast to these low methane yields with iron catalysts, nickel usually produced 900- to 1,000-B.t.u. product gases at estimated calorific efficiencies that nearly always approached 100 percent.

With almost all of the iron catalysts tested, carbon deposition was excessive, even with synthesis gases having hydrogen-carbon monoxide ratios as high as 2.5. In contrast to this, very little carbon deposited on nickel catalysts when hydrogen-carbon monoxide ratios of 2.5 were used. With synthesis gas having a hydrogen-carbon monoxide ratio of 1, it was almost impossible to continue experiments for any extended period of time with either iron or nickel catalysts because of carbon deposition.

The major effect of changes in space velocity with nickel catalysts was reflected in the temperature profiles of the catalyst bed. In figure 15, the temperatures at various heights within the catalyst bed are plotted as functions of the distance from the top of the reactor and space velocity. The catalyst that was used for this test was an extracted Raney-nickel alloy. A three-fold increase in space velocity shifted the peak temperature in the bed only 1 inch further down in the bed, indicating that the activity of the catalyst was quite high.

Later manipulations of the space velocity with this same catalyst resulted in a steady decrease of the temperature gradient within the catalyst bed. In the period just before termination of the run, a temperature difference of about 10° C. in the length of the bed was observed at a space velocity of 1,500 hr.$^{-1}$. The synthesis gas conversion at this time was over 90 percent, and the heating value of the product gas was better than 900 B.t.u. per cu. ft.

22/ Space velocity = $\dfrac{\text{Volumes of gas per hour (NTP)}}{\text{Volume of catalyst bed}}$.

TABLE 1. - Mixed-bed experiments

Catalyst composition and pretreatment	Catalyst number	H2/CO ratio	Temperature range, °C	Pressure range, p.s.i.g.	Space velocity range, hr.-1	Temp., °C	Pressure, p.s.i.g.	CH4 vol., percent	Heating value,[2] B.t.u./s.c.f.	Calorific efficiency, percent	Termination of run due to-
							Best methanation conditions				
Chosen iron ore - reduced	D-6022	1	251-321	0-300	100-300	321	300	37.5	896	52	Excessive carbon.
Cuhan iron ore - reduced	D-5022.2	2	324-372	300	100-360	358	300	34.4	765	59.9	Sufficient data.
Fused Fe3O4, reduced and nitrided N/Fe = 0.44	L-1022	2	248-395	300	100-330	395	300	30.5	738	97.2	Excessive carbon.
Fe3O4 (50%) and ball clay, reduced and nitrided N/Fe = 0.48.	L-1038	2	246-310	0-300	200-300	322	300	27.5	591	63.5	Do.
Fe2O3,Al2O3 ppt. on kaolin - reduced	L-6038	2.5	348-353	300	300	348	300	12.7	(440)	NC	Do.
Fe-Ni-MgO-SiO2 (53.8:12.4:2.1:0.2) N/Fe = 0.314, reduced and nitrided	L-3047	1	240-280	300	300	273	300	39.7	706	69.5	Sufficient data, some carbon.
Ni, ThO2-Cr2O3 ppt. or kieselguhr (30.5:7.6:1.6:59.9) - reduced	L-6008	1	230-330	0-300	100-300	328	0	60.8	785	64.2	Excessive carbon.
10% Ni impregnated or steam-treated cracking catalyst base - reduced	L-6013	1	300+	300	300		No appreciable activity				
5% Ni impregnated on cracking catalyst base - reduced	L-6014	1,2	316-402	300	300	398	300	44.6	874	64.3	Do.
4.8% Ni on Al2O3 (Girdler catalyst) - reduced	L-6016	1	320-396	0-100	100	382	100	24.9	NC	NC	Do.
10% Ni impregnated on cracking catalyst base - reduced	L-6017	1	300+	300	300		No appreciable activity				
5% Ni impregnated on cracking catalyst base plus K2O-reduced	L-6019	2.5	400	300	300	400	300	39.1	535	NC	Do.
1% Ni impregnated on activated charcoal - reduced	L-5020	1	318-406	300	100-300		No appreciable activity				
10% Ni ppt. or silica gel (6% Ni) - reduced	L-6023	1	250-360	0-300	300	344	300	41.4	789	64.2	Do.
NiO-Al2O3 ppt. on kaolin (100:200:125) - reduced	L-6024	1	320-360	300	100-300	355	300	48.3	(720)	NC	Do.
NiO-Al2O3 ppt. on kaolin (100:200:125) - reduced	L-6025	2	300-309	300	300	300	300	99.9	1077	NC	Do.
NiO-Al2O3 ppt. on kaolin (100:200:125) - reduced	L-6025.3	2	213-410	300	300	351	300	96.9	(2050)	NC	Decreased activity.
NiO-MgO ppt. on kaolin (100:200:125) - reduced	L-6034	2,2.5	210-340	300	300	300	300	97.5	(1060)	NC	Sufficient data.
29% Ni, 5.5% Mi, 2.4% Al ppt. on kaolin - sintered and reduced	L-6036	2.5	300+	300	300	264	300	97.3	(1060)	NC	Sufficient data, decreased activity.
32% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin - recuced	L-6036.1	2.5	274-290	300	300-400	274	300	94.4	(1035)	NC	Sufficient data.
NiO, MnO ppt. on Norton alumina pellets - reduced	L-6040	2.5	400	300	300	400	300	30.3	(560)	NC	Do.
NiO, MnO, Al2O3 ppt. on cracking catalyst - reduced	L-6041	2.5	400-405	300	300	404	300	17.3	(440)	NC	Do.
NiO-Al2O3 ppt. on Norton cylinders (5.8% Ni) - reduced	L-6044	2.5	290-400	300	300-700	346	300	94.2	(1030)	NC	Insufficient activity.
NiO-MnO2, Al2O3 ppt. on zirconia cement - reduced	L-6052	2.5	300-305	300	300-500	300	300	94.8	(1030)	NC	Sufficient data, decreased activity.
Ni pellets steam-treated - reduced	L-6048	2.5	400	300	100-300		No appreciable activity				Decreased activity.
Raney cobalt, 40% Co, 60% Al, steam-treated - reduced	L-6049	2.5	300+	300	300		No appreciable activity				
Raney cobalt (50% Co, 50% Al), Al partly extracted with NaOH	L-6049	2.5	280-316	300	300-2,900	286	300	92.1	(1050)	NC	Excessive carbon.
Raney nickel (44% Ni, 56% Al), steam-treated - reduced	L-6054	2.5	300+	300	300		No appreciable activity				
Raney nickel (44% Ni, 56% Al), Al partly extracted with MnOH	L-6058	2.5	280-302	300	300-1,500	300	300	96.9	(1060)	NC	Sufficient data.

1/ CO2, H2O free.   2/ ( ) estimated.   NC = Not calculated.

Catalyst L-6058
Extracted Raney Nickel

Period	SVH	Dowtherm bath temp.
1 ×····	300 hr.$^{-1}$	302° C.
2 o····	600 hr.$^{-1}$	299° C.
3 •	1,000 hr.$^{-1}$	299° C.
4 □	600 hr.$^{-1}$	300° C.

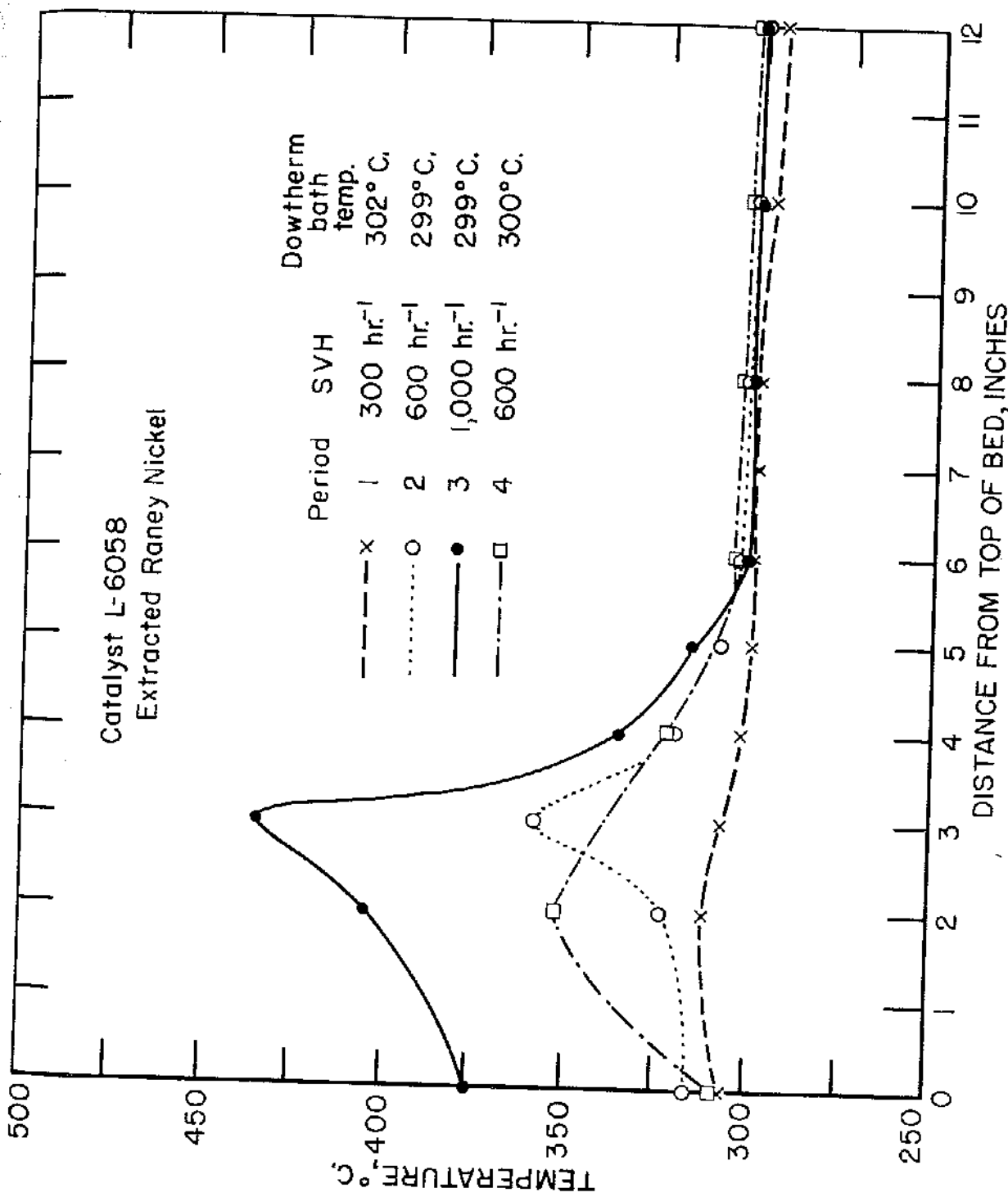TEMPERATURE, °C.

DISTANCE FROM TOP OF BED, INCHES

Figure 15. - Effect of space velocity on temperature profile.

Discussion

Despite the fact that these tests show that nickel materials are much superior to iron materials as methanation catalysts, it must be realized that the industrial production of high-B.t.u. fuel gas can also be considered in terms of a combined process producing both liquid and gaseous products, in which case, iron and hot nickel would probably be the most suitable material. If iron is used, however, carbon deposition would be a major problem in the process, since increases in hydrogen-carbon monoxide ratios are not sufficient to prevent deposition. Other techniques, such as addition of steam suggested by the Gas Research Board,[23] might be a partial solution to this problem, and attempts were made to evaluate the effectiveness of this method in the fluidized-bed work that is discussed in a later section of this paper.

One of the major results of the fixed-bed studies was a clue to the order of magnitude of the reaction rates within the nickel catalyst beds, which was obtained from the measurement of the temperature distributions within the reactor. This phenomenon of high reaction rates was a problem that proved to be a major difficulty in the fluidized-bed studies since the high rate of conversion of synthesis gas at high space velocities produced large quantities of heat and resulted in excessive temperature gradients in the catalyst bed.

The use of Raney alloys is to the authors' knowledge, the first successful attempt at using these alloys as dry-bed hydrogenation catalysts.[24] Although a great deal more work must be done before the utility of these materials is completely evaluated, the preliminary results indicate that these extracted alloys might be used successfully for methanation in large-scale, fixed-bed equipment.

FLUIDIZED-BED TESTING

Two types of fluidized-bed design were used to carry out the bench-scale phase of the work. A conventional single-feed static fluidized reactor was used to evaluate iron catalysts. However, it was observed that the heat-transfer characteristics of this unit were inadequate to handle the quantity of heat evolved during the tests with nickel catalysts, and when excessive temperatures damaged the unit, a multiple-feed static fluidized unit was designed and constructed. Each unit and the results obtained from that unit will be discussed separately.

Conventional Bed

Equipment Description

The fluidized unit that was used for evaluating iron catalysts is shown schematically in figure 16. The reactor consists of a 3/4-inch, Schedule 80, seamless, steel pipe 6 feet in length enclosed in a 2-inch, Schedule 40, Dowtherm heat-exchanger jacket. A one-fourth-inch finned baffle tube is inserted in the center of the reactor tube to disperse the catalyst and aid in fluidization and to serve as a well for the thermocouples that are used to measure catalyst-bed temperatures. The reactor head is fitted with two stainless-steel porous filters, which are shown in figure 17, to prevent the carry over of small catalyst particles with the product gas. The filters are arranged so that one may be used to remove product gas

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[23]/ See work cited in footnote 10.
[24]/ Fischer, F., and Meyer, K., Suitability of Alloy Skeletons as Catalysts for Benzine Synthesis: Brennstoff-Chem., vol. 15, 1934, pp. 84, 107.

POROUS METAL
FILTERS

MULTIPLE THERMOCOUPLE
WELL & BAFFLE TUBE

DOWTHERM JACKET

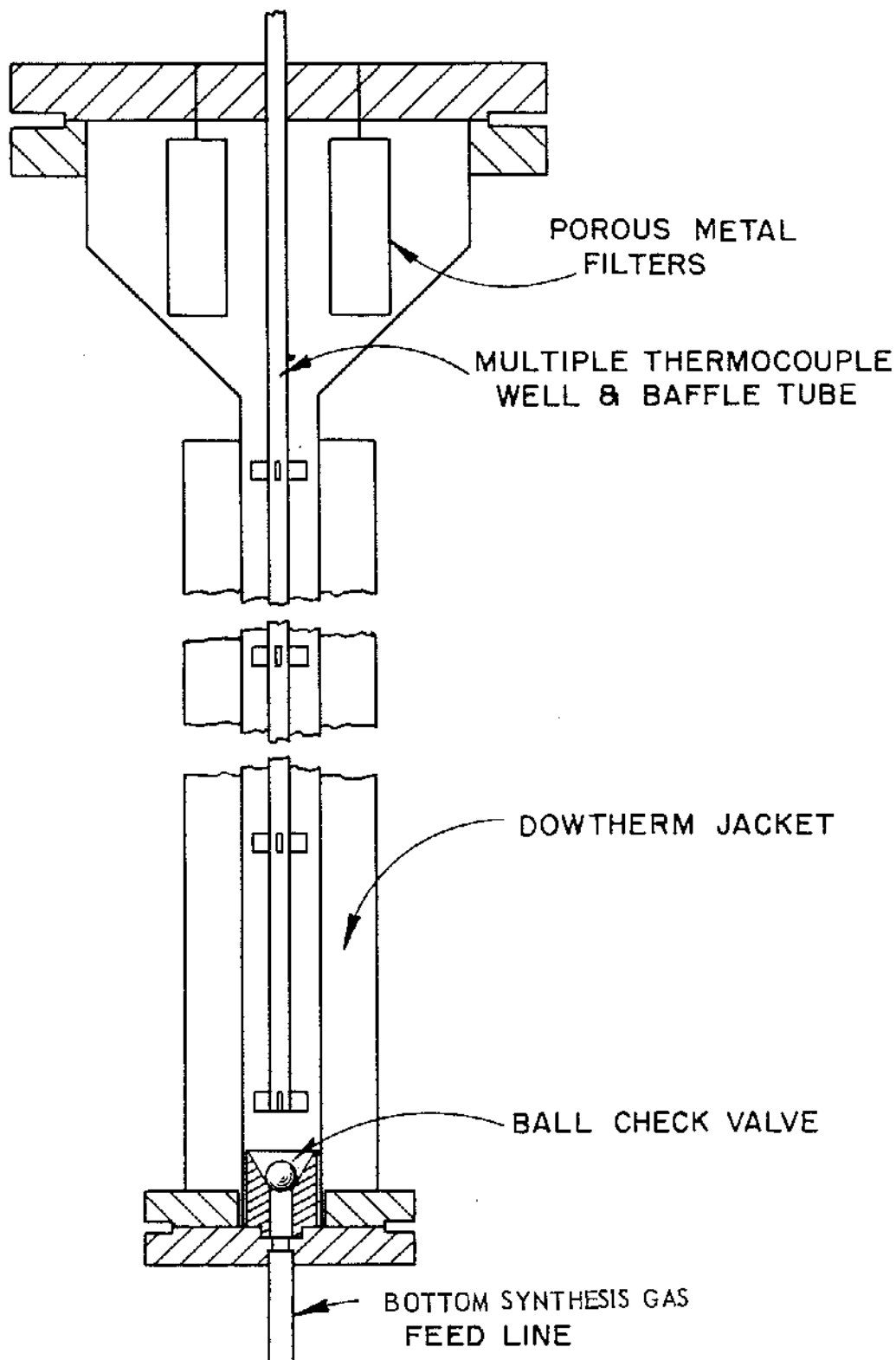BALL CHECK VALVE

BOTTOM SYNTHESIS GAS
FEED LINE

Figure 16. - Conventional fluidized-catalyst reactor.

Figure 17. - Filter and baffle tube, fluidized bed.

while the other is being cleaned and cooled by a stream of blowback recycle gas. The bottom of the reactor tube is fitted with a ball-valve unit to prevent catalyst from settling into the bottom flange section of the unit. Provision is made to sample catalyst through the bottom of the reactor during operation by displacing the ball with a rod and allowing catalyst to drop into a small-diameter capped pipe that extends below the bottom flange. This arrangement is not shown in figure 16.

A flow diagram for this unit is shown in figure 18. Synthesis gas at 400-600 p.s.i.g. is supplied to the reactor from the high-pressure manifold through a main shutoff valve, pressure reducer, rotameter, and gas preheater. The activated charcoal trap shown in figure 18 was not installed until after the work with iron catalysts was completed. Steam may be added to the synthesis gas by passing the synthesis-gas stream through an electrically controlled saturator placed ahead of the preheater. Provisions are also made to supply the system with hydrogen for reducing and ammonia for nitriding catalysts.

Product gases are passed through a trap system to recover liquid and solid products, after which the stream is divided, one portion going to a recycle compressor and the other through a back-pressure regulator to a gas meter, a recording CO_2 analyzer, a recording-indicating calorimeter, and out to atmosphere. The recycled gases pass through a rotameter and join the synthesis-gas line just before the saturator. A small amount of recycle gas is used to provide blowback gas for the filters.

A manometer is placed across the unit, between a point in front of the preheater and a point after the filters, to measure pressure drops across the bed during operation.

The reactor is heated by electrical coils that are placed around the heat-exchanger walls. In addition to these heaters, auxiliary heaters are used at the bottom- and top-flange sections of the reactor to compensate for heat losses at these points. A separate temperature controller regulates the temperature of the bottom-flange section. Temperatures of various points within the catalyst bed are measured by iron-constantan thermocouples and are recorded on a recording-indicating potentiometer.

The temperature and pressure limits of the unit are approximately $450°$ C. and 400 p.s.i.g., respectively. At these operating conditions, based upon a maximum gas-fluidization velocity of approximately 2 ft. per sec., a total flow of fresh-feed and recycle gas of about 200 std. c.f. per hr. and a recycle to fresh-feed ratio of about 3:1 can be obtained. In normal operation, the unit holds about 300-400 cc. of catalyst with particle size less than 80-mesh (U.S.S.), which yields a settled catalyst-bed height of 3-4 feet. During normal operation (linear gas velocity $\sim$ 1 ft. per sec.), a bed expansion of approximately 50-percent is obtained. All space velocities, however, are calculated on the basis of settled volume of raw catalyst.

Operating Procedures

The catalyst to be charged to the reactor was crushed to a size smaller than 80-mesh before being placed in the reactor. Other than this no attempt was made to select a predetermined size distribution, unless a particular catalyst was run a number of times. Table 2 is a summary of the particle-size characteristics of the iron catalysts used in the conventional-bed studies.
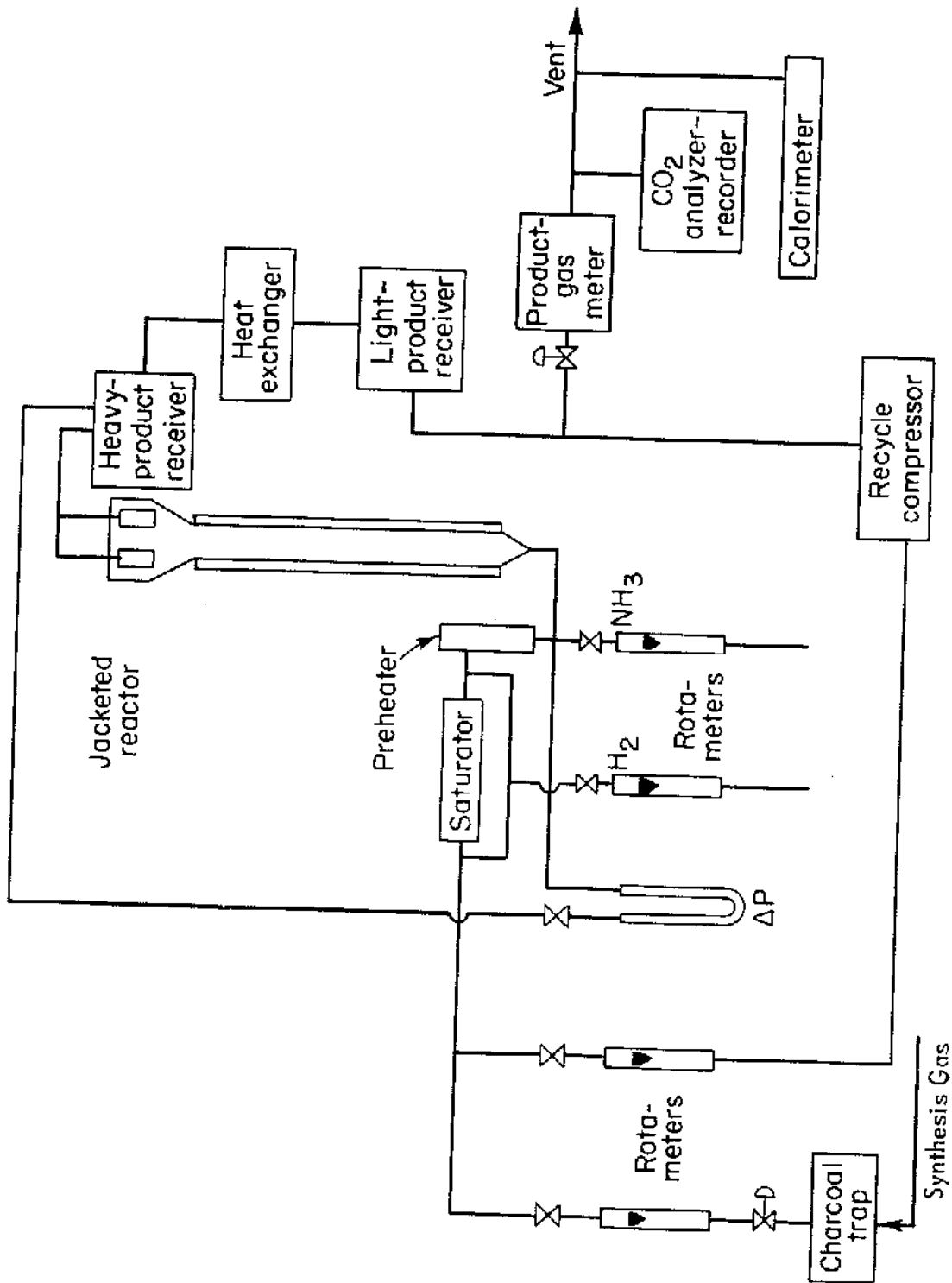
30

Figure 18. - Conventional fluidized-catalyst reactor flow diagram.

The catalyst was reduced at 350°-400° C. and 100 p.s.i.g., with maximum re-
cycle gas and minimum fresh-feed hydrogen. Water was removed before passing the
exit gases from the reduction to the recycle compressor. The extent of reduction
and nitriding of the catalysts have been discussed previously.

TABLE 2. - Sieve analysis of iron catalysts

Catalyst number	D-3001	D-1033	D-1034		L-1026
Catalyst volume, cc.	350	300	340	350	350
Catalyst weight, gm.	800	853	748	807	717
Sieve analysis, percent by wt.:					
>80	0.00	0.00	0.00	0.00	0.00
80-115	30.4	32.3	1.50	17.7	23.0
115-150	13.0	21.5	28.4	7.80	7.30
150-170	14.1	6.72	15.8	23.5	36.4
170-200	13.4	6.72	15.8	23.5	4.80
200-250				11.8	
	}29.1	}32.7	}38.5		}28.5
250				31.4	

The bed was heated to 200° C. to prevent formation of metal carbonyls before
the initiation of synthesis. The temperature was increased slowly from 200° C. to
the temperature at which a minimum feed-gas volume contraction of 60-70 percent on
a water- and carbon dioxide-free basis was obtained. If this contraction was not
obtained at the initial operating pressure, the temperatures were reduced to 200° C.,
the pressure was increased, and the temperature was slowly increased again. When
the desired volume contractions were obtained, spot samples of the product gas were
taken for analysis. Catalysts were generally studied in the temperature and pres-
sure ranges of 200°-400° C. and 0-300 p.s.i.g, respectively.

Results of Iron-Catalyst Tests in Conventional Bed

The results of the tests with iron catalysts are summarized in table 3. All of
these materials produced large quantities of carbon with synthesis gases having a
hydrogen-carbon monoxide ratio of 1. Although there was some decrease in the quan-
tity of carbon deposited when the ratios were increased to 3, the amount of carbon
deposited at the higher ratios was still excessive and it was difficult to obtain
satisfactory process data.

It was extremely difficult to obtain product gases having heating values
greater than 700 B.t.u. per cu. ft., and, with all of the catalysts, the yields of
C_3 + hydrocarbons were high. These high yields of C_3 + hydrocarbons were responsi-
ble for the low calorific efficiencies obtained with iron catalysts. The least
desirable catalyst with respect to these high yields of C_3 + hydrocarbons was a
reduced and nitrided synthetic ammonia catalyst (D-3001), which produced a gas hav-
ing a heating value of 800 B.t.u. per cu. ft., but at a calorific efficiency of
less than 45 percent.

The best iron catalyst was a reduced and nitrided fine steel shot (D-1034),
which is a byproduct of steel-shot manufacturing. This material was subjected to
a number of tests to determine its synthesis characteristics. Figure 19 shows the
effects of temperature on the composition and on gross heating value of the product
gas obtained when using this catalyst at a pressure of 100 p.s.i.g., a recycle ratio
of 2:1, a fresh-feed space velocity of 840 hr.-1, and a synthesis gas having a hy-
drogen-carbon monoxide ratio of 1. The results of additional tests to determine the

TABLE 3. - Fluidized-bed iron catalyst evaluation

| Catalyst name and number	Catalyst composition			Feed gas composition	Fresh feed space velocity range, hr.$^{-1}$	Recycle ratio, R:F	Temp. range, °C.	Pressure range, p.s.i.g.	Results of experiments
	Before pretreatment	Pre-treatment	After pretreatment						
Synthetic ammonia Catalyst - D-3001	Fe$_3$O$_4$:MgO+K$_2$O 10:1	None	-	$\frac{H_2}{CO} = 1$	3,000	2:1	to 324	100	Excessive carbon.
		Reduced and nitrided	ε-Fe$_2$N(90+%) and Fe$_3$O$_4$	$\frac{H_2}{CO} = 1+$ 5% CO$_2$	800 to 840	2:1	to 300	100	Excessive carbon and C$_3$ + hydrocarbons.
Alan Wood magnetite D-2033	Fe$_3$O$_4$	None	-	$\frac{H_2}{CO} = 1$	1,700	2:1	to 400	100	Excessive carbon.
Scrap-steel shot fines, D-1034	69% Fe, 6.50% Si, 0.47% C, 0.23% S	Reduced and nitrided	α-Fe, ε-Fe$_2$N	$\frac{H_2}{CO} = 1$	840	2:1	287 to 350	100	690-B.t.u. product gas.
			α-Fe, ε-Fe$_2$N, γ-Fe$_4$N	$\frac{H_2}{CO} = 3$	1,940 to 3,100	1:1 to 3:1	340 to 350	230 to 275	760-B.t.u. product gas at calorific efficiency of 70%.
			α-Fe, ε-Fe$_2$N	$\frac{H_2}{CO} = 2.5$	3,630 to 14,500	0	320 to 350	300	570-B.t.u. product gas at calorific efficiency of 51%.
				$\frac{H_2}{CO} = 2.5$	1,850 to 3,700	1:1 to 3:1	340	300	630-B.t.u. product gas at calorific efficiency of 63%.
				$\frac{H_2}{CO} = 2.5$ 2.6% steam	1,800 to 4,300	0 to 4:1	340	300	720-B.t.u. product gas at calorific efficiency of 65%.
Sintered magnetite and ball clay, L-1026	85% Fe$_3$O$_4$, 15% ball clay	Reduced and nitrided	ε-Fe$_2$N, Fe$_3$O$_4$, SiO$_2$	$\frac{H_2}{CO} = 3$	880	2:1	300 to 400	100 to 200	767-B.t.u. product gas, excessive carbon.
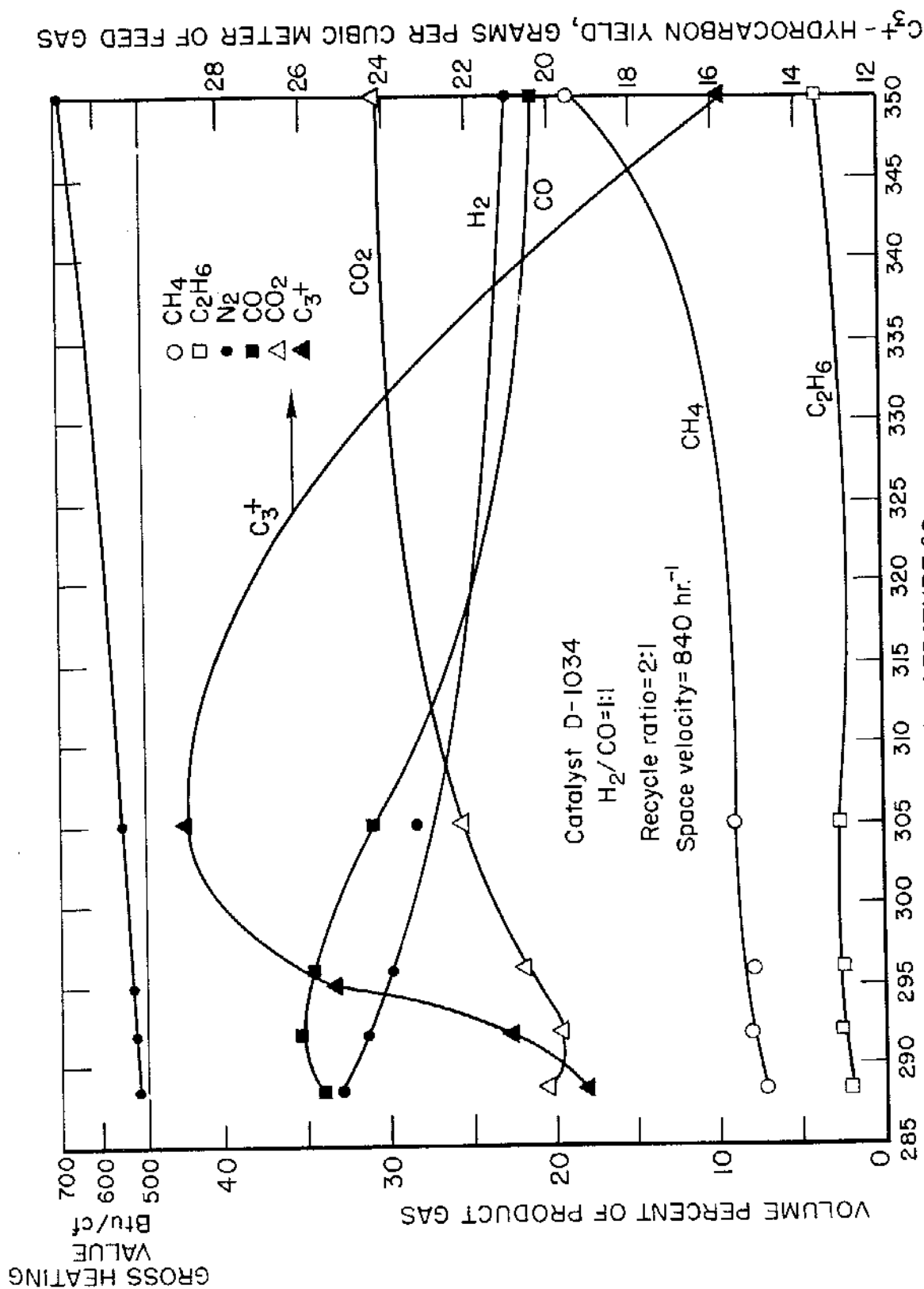
Figure 19. - Effect of temperature on products; 100 p.s.i.g.