SYNTHESIS OF METHANE IN HOT GAS RECYCLE REACTOR--PILOT PLANT TESTS

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INTRODUCTION

Development of large-scale catalytic methanation reactors is necessary to complete the commercialization of plants for converting coal to substitute natural gas. Major objectives in developing a catalytic methanation system are to achieve efficient removal of the heat of reaction so as to minimize thermal deactivation of catalyst and to minimize catalyst deactivation by other causes such as chemical poisoning and structural changes. The hot gas recycle reactor, where large quantities of partially cooled product gas are circulated thru the catalyst bed, affords one satisfactory method of removing large amounts of heat from the catalyst surface. Early Bureau of Mines experiments with the hot gas recycle reactor, however, had short catalyst lives, on the order of 200 hours.(1) [1] The work described in this report attempts to extend the life of the catalyst in the hot gas recycle reactor system, to determine the effects of some of the process variables, and to compare the performance of a bed of pelleted nickel catalyst against that of a bed of parallel plates coated with Raney nickel.

PILOT PLANT DESCRIPTION

The reactor in the hot gas recycle pilot plant was constructed of type 304 stainless steel 3 inch schedule 40 pipe, 10 feet long, flanged at each end. In three experiments (HGR-10, 12, and 14), the catalyst bed consisted of grid assemblies of parallel, type 304 stainless steel plates, that had been flame spray coated with Raney nickel. The grid assemblies, each 6 inches long, were stacked to the desired bed height and conformed to the inside diameter of the reactor. Grid plates were aligned perpendicular to the plate alignment of adjacent grids. Prior to assembly, each plate was sand-blasted on both sides, flame sprayed with a bond coat, and finally flame sprayed with the Raney nickel catalyst. Thickness of the Raney nickel coating was approximately 0.02 inches. In experiment HGR-13, the reactor was charged with 1/4" pellets of a commercial grade precipitated nickel catalyst instead of the parallel plates coated with Raney nickel. Physical properties of the catalyst beds are shown in table 1.

The basic hot gas recycle reactor scheme is shown in the simplified flowsheet of figure 1. The main reactor containing the parallel plate grid assemblies is the one under study in this report. The second stage reactor, an adiabatic reactor charged with a precipitated nickel catalyst, was operated at intermittent periods; its operation will be discussed in a later report. Additional heat exchangers, not shown in the flowsheet, were used in the pilot plant to compensate for system heat losses, to achieve a measure of heat recuperation, and to control the gas temperature into the hot gas compressor and into the main reactor. Cooling of the main catalyst bed is achieved by direct transfer of the reaction heat to the slightly cooler gas stream flowing through the bed. Recycle stream is appropriately cooled before returning to the reactor. The hot recycle stream may be cooled either directly without condensation or by cooling a portion of the recycled product gas sufficiently to condense out the water vapor and then returning the resulting cold recycle gas along with the hot recycle gas. After undergoing a final heat exchange, the mixture of the cooled recycle gas and the fresh feed gas comprise a feed to the hot gas recycle


1/ Underlined numbers in parenthesis refer to references at the end of this paper.

reactor at a controlled temperature that may be 50 to 150° C lower than the reactor outlet temperature, depending upon the total amount of gas recycled and the amount of heat exchange.

Charcoal absorption towers (not shown in the flowsheet) were used to keep the sulfur content in the fresh feed gas to less than 0.1 ppm. in equivalent volume of H_2S.

CATALYST PREPARATION

The metal plates to be coated with Raney nickel were type 304 stainless steel. The surfaces of the plates were prepared by sand-blasting with an iron-free grit and then flame spraying on a light coat of bonding material, about 0.006 inches thick. After the surface was bond coated, the Raney nickel alloy powder (80-100 mesh) was flame sprayed on to the desired thickness. The plates were assembled in parallel, inserted in the reactor, and then activated. Activation of the Raney nickel involved passing a 2 wt. per cent solution of NaOH through the catalyst bed to dissolve away the aluminum phase and leave a spongy surface of highly active free nickel. Activation was stopped after 70 per cent of the aluminum in the Raney alloy was reacted. The remaining unreacted alloy is believed to provide a base upon which the activated nickel remains anchored. The extent of reaction was determined by measuring the hydrogen evolved according to the following three reactions, all of which evolve 3 moles of H_2 for every 2 moles of Al reacted:

$$2 Al + 2 NaOH + 2 H_2O \rightarrow 2 Na AlO_2 + 3 H_2$$

$$2 Al + NaOH + 4 H_2O \rightarrow NaAlO_2 + Al(OH)_3 + 3 H_2$$

$$2 Al + 3 H_2O \rightarrow Al_2O_3 + 3 H_2$$
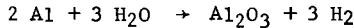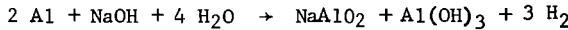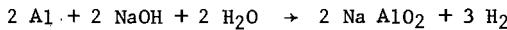
After the aluminum was reacted, the catalyst was washed with water which had a pH of about 6.8 until the pH of the effluent water reached about 7.2. After the catalyst was activated and washed, it was always kept under a hydrogen atmosphere until it was put into methanation service at the desired operating pressure and temperature. Before cooling the catalyst to take it out of service, the reactor was purged with hydrogen. It was kept in a hydrogen atmosphere during cooling, depressurizing, and stand-by condition.

In experiment HGR-13, the commercial grade precipitated nickel catalyst was in a reduced and stabilized condition when it was charged into the reactor. No special activation treatment was needed. It was, however, kept under a hydrogen atmosphere at all times until the temperature and pressure of the system was brought to synthesis conditions at which time the synthesis feed gas was gradually fed into the system to start the run.

PROCEDURES AND RESULTS

General

Experiments HGR-10, 12 and 14 were conducted with the flame sprayed Raney nickel catalyst. Experiment HGR-13 used the pelleted precipitated catalyst to compare its performance with that of catalyst used in HGR-14. Reactor conditions as a function of stream time for experiments HGR-10, 12, 13, and 14 are graphically presented by computer print-out in figures 2, 4, 6, and 8, respectively. Corresponding carbon monoxide concentrations and heating values of the product gases and the yields of methane produced per pound of catalyst used are presented graphically as a function

of stream time in figures 3, 5, 7, and 9. The total recycle ratio was calculated on
the basis of stream analyses, and fluctuated widely because of the high sensitivity
of the calculated values to small changes in stream analyses. All runs were made at
300 psig.

The major process parameters are presented in tables 2, 3, 4, and 5 at selected
periods in experiments HGR-10, 12, 13, and 14, respectively. Carbon recoveries shown
for these periods ranged from 63 per cent to 91 per cent. Most of the losses occurred
in connection with the recycle compressor system and correspondingly decreased the
volume of product gas metered. Such losses, however, did not significantly affect
the incoming gas to the main reactor or the performance of the reactor.

Experiment HGR-10

Experiment HGR-10 operated at 300 psig with recycle ratios being varied to give
temperature rises across the catalyst bed ranging from 50° to 150° C. Temperature
control was excellent. Total operating time was relatively short at 910 hours. The
initial carbon monoxide concentration in the product gas at 0.3 per cent was higher
than the desired value of less than 0.1 per cent. Over the entire experiment, the
average rate of catalyst deactivation, expressed as increase in the per cent carbon
monoxide in the dry product gas per mscf methane produced per pound of catalyst
charged, was 0.23 per cent/mscf/lb. This is a high rate of deactivation compared
with the value of about 0.009 per cent/mscf/lb. obtained with Raney nickel catalyst
in a tube-wall methanator test (TWR-6). (2) Because the experiment was of short
duration, the resulting production of methane per pound of catalyst in HGR-10 was
low at about 11.8 mscf/lb. as compared with 177 mscf/lb. in tube-wall reactor test
TWR-6.

One probable reason for the relatively poor catalyst performance in experiment
HGR-10 was the excessively large deposits of iron and carbon on the catalyst surface.
Table 6 shows iron and carbon concentrations of 22.0 and 13.4 weight per cent, re-
spectively, on the catalyst near the gas inlet, and 0.8 and 1.9 weight per cent,
respectively, on the catalyst near the gas outlet. It is suspected that the large
deposit of iron resulted from the decomposition of iron carbonyl carried in from
other parts of the reactor system, and the deposited iron in turn favored the forma-
tion of free carbon from the incoming carbon monoxide.

Experiment HGR-12

As shown in table 1, the catalyst bed for experiment HGR-12 was the same as
that used in experiment HGR-10, except that the coat of Raney nickel used in HGR-12
was slightly thinner than that used in HGR-10. The objective in HGR-12 was to in-
crease catalyst life. The methane produced per pound of catalyst was 39.5 mscf af-
ter a total operating time of about 1400 hour (See figure 5). The overall average
rate of catalyst deactivation, 0.091 per cent per mscf per lb., was about 40 per cent
of that for experiment HGR-10, but still 10 times greater than that of experiment
TWR-6. The carbon monoxide concentration in HGR-12 increased from 0.1 per cent at
the start of the experiment, to 3.7 per cent at the end of the experiment.

In general, the rate of deactivation was much lower at the lower fresh gas feed
rate than at the higher feed rates. For example, during the period between 600
hours and 800 hours stream time, at the lower feed rate of about 206 scfh, the rate
of deactivation was 0.022 per cent/mscf/lb. as compared with a deactivation rate of
0.143 per cent/mscf/lb. for the period between 100 hours and 400 hours where the
fresh feed rate was about 386 scfh.

The cold gas recycle ratio values shown in figure 4 are metered values and are more consistent than the hot gas recycle and total gas recycle ratio values which, as explained earlier, were calculated from gas analyses. Although the calculated total recycle gas flow rate was erratic, the catalyst bed temperatures were uniform and easily controlled by varying the recycle rate and its temperature level. The uniformity of the catalyst bed temperature, as shown by figure 4, indicates that the actual recycle rate was much more uniform than indicated by the calculated values. The data plotted in figures 4 and 5, indicate that between the stream time of 260 hours and 460 hours, raising the maximum temperature of the catalyst bed from 350° C to 410° C did not significantly change the trend of increasing carbon monoxide concentration in product gas. However, this trend in carbon monoxide concentration was reversed during the subsequent period between 467 and 539 hours when the carbon monoxide concentration in the product gas decreased from 2.0 to 1.7 per cent (dry). This decrease in carbon monoxide concentration is attributed mainly to the ratio of total recycle gas to a fresh gas being decreased from about 20:1 to about 8:1 with an attendant increase in residence time. The decrease in total recycle ratio was achieved by reducing the hot gas recycle ratio to about 5:1 while leaving the cold gas recycle ratio constant at 3:1. The water vapor concentration in the mixed feed to the reactor correspondingly was decreased slightly from 5.5 per cent to 3.7 per cent and the resulting temperature spread across the catalyst bed increased from about 51° C to 112° C. Table 3 shows the wet analyses of the product gas during operation with the lower recycle ratio of 8:1 at 539 hours stream time.

After experiment HGR-12 was ended, samples of the spent catalyst were taken from various locations in the bed, and surface areas (B.E.T.), pore volumes and distribution of pore radii were determined for each sample. The results are shown in table 7 as a function of distance from the gas inlet end of the catalyst bed. Additional catalyst information such as x-ray analysis, chemical analysis, and metal surface area determined by chemisorbed hydrogen are presented in table 8 for spent catalyst at the gas inlet and outlet. The B.E.T. surface areas are about one-half that of freshly activated Raney nickel where the surface area is as high as 64 m^2/gm.

Special catalyst activities expressed as per cent CO converted to methane were determined in a thermogravimetric analyzer for samples of spent catalyst taken at 0, 6, and 60 inches from the gas inlet; corresponding CO conversions were 0.0, 0.9, and 18 per cent. The catalyst nearest the gas outlet--when compared with catalyst at the gas inlet--was the most active and had the lowest carbon content, the larger pore radii with 96 per cent of its pore volume having radii greater than 60 Å, the lowest B.E.T. surface area (19.5 m^2/gm) and the largest free metal surface (4.9 m^2/gm). These observations are all consistant if one assumes that the combination of finer pore structure and higher B.E.T. surface area found at the gas inlet side of the bed is indicative of a higher carbon concentration and that the nickel pore radii are larger than that of the amorphous carbon deposit.

Experiment HGR-13

In experiment HGR-13, a two foot bed of commercial catalyst was tested as a packed bed of 1/4 inch pellets. (See table 1 for bed properties). This test was made for comparison with a similar test (HGR-14) using a catalyst bed of parallel plates sprayed with Raney nickel. The experiment also was to show the effect of varying the fresh feed rate from a space velocity of 2000 to 3000 hours $^{-1}$,where space velocity is based on scfh of gas at 1 atm and 32° F per cubic foot of catalyst bed.

Major process conditions for experiment HGR-13 are plotted against stream time in figure 6. The total recycle ratio was held relatively constant at about 10:1 resulting in a constant temperature-rise of about 100° C across the catalyst bed

(300° C at the inlet and 400° C maximum). Near the end of the experiment, the cold recycle ratio was varied between the value of 8:1 and 1:1. The experiment was ended at 1368 hours.

As shown in figure 7, the carbon monoxide concentration in the dry product gas ranged from about 0.02 per cent at the start to 1.2 per cent at 840 hours, and decreased to 0.88 per cent at 1368 hours, at the end of the run. The total methane produced per lb. of catalyst was about 11.5 mscf/lb. Heating value of the product ranged from 885 to about 960 Btu/scf.

The overall deactivation rate expressed as per cent carbon monoxide increase per mscf methane produced per pound of catalyst was about 0.076. During the course of the experiment, as the fresh gas rate was varied from about 210 scfh to 320 scfh and finally back to 210 scfh, deactivation rates corresponding to those feed rates were 0.014, 0.222 and 0.079. Thus, the deactivation rate was increased irreversibly by increasing the fresh gas rate.

Typical operating data from selected periods in experiment HGR-13 are presented in table 4. Period 6, 168 hours stream time, is typical of conditions at the initial part of the experiment while period 54 is representative of conditions at the end of the experiment. Comparison of period 20 with period 6 indicates that very little change in performance occurred over that span of 336 hours of operation; for example, the decrease in conversion of $(CO + H_2)$ in the fresh feed gas was very slight, decreasing from 98.0 per cent to 97.9 per cent. Comparison of period 20 with period 22, shows typical effects of increasing the fresh feed rate from a space velocity of 2110 hr^{-1} to 3020 hr^{-1}. Conversion of $H_2 + CO$ in the fresh feed, for example, dropped from 97.9 per cent to 97.1 per cent. Data in period 34 shows a further drop in performance which may be attributed to continued operation at the higher fresh feed rate of 320 scfh or space velocity of 3120 hr^{-1}.

After the fresh feed rate was returned to the lower rate of 211 scfh, a comparison of carbon monoxide in the product gas in period 37 (0.4 per cent) with that in period 20 (0.1 per cent) shows that the catalyst had definitely lost activity with time. However, this activity loss is not evident in the respective heating values of 933 and 926 Btu/scf, for periods 37 and 20 because the product gas in period 37 was less diluted with excess hydrogen than was the product gas in period 20. This is confirmed by the H_2/CO in the fresh feed gas; $H_2/CO=3.01$ for period 37 and 3.24 for period 20.

X-ray defraction analysis of the spent catalyst presented in table 8 show the nickel to be present only in the metallic state. Chemical analyses also presented in table 8 indicate very little difference in composition of catalyst at the gas inlet and at the gas outlet.

Experiment HGR-14

The reactor was packed with 2 feet of parallel plates sprayed with Raney nickel as described in table 1. Spraying and activation of the catalyst was the same as described under catalyst preparation. Operating conditions were maintained practically the same as they were for experiment HGR-13, except for the periodic changes in the cold gas recycle ratio. Figure 8 shows reactor conditions in experiment HGR-14 as a function of time on stream and figure 9 presents the resulting carbon monoxide concentration, heating values, and methane produced per pound of catalyst.

At the start of the experiment, the carbon monoxide concentration in the product gas was very low, less than 0.01 per cent. The unusually high value (0.71 per cent) shown at 186 hours stream time is due to analytical error. At the end of the experiment, after 2307 hours stream time, carbon monoxide in the product gas had increased

to 0.93 per cent (dry basis) and total methane produced per pound of catalyst was 32 mscf/lb.

The average catalyst deactivation rate over the entire experiment was 0.0291 per cent/mscf/lb. The rate of deactivation during the initial 462 hours operation at a fresh feed space velocity of about 2090 hr^{-1} (216 scfh) was very low at 0.0017 per cent/mscf/lb.; from about 500 hours to 841 hours at about 2990 hr^{-1} space velocity, the rate of deactivation increased to 0.040 per cent/mscf/lb. Catalyst deactivation rates during HGR-14 are shown below for various operating periods and fresh feed space velocities:

Nominal Fresh Feed Space Velocity, hrs^{-1}	Stream Period, hrs From	To	Catalyst Deactivation Rate, per cent/mscf/lb
2000	0	462	0.00166
3000	462	841	0.0396
2000	841	1058	0.0027
2000	1058	1760	0.0187
2000	1760	2180	0.0821

As noted previously in experiment HGR-13, the deactivation rate increased signifi-cantly when the fresh feed space velocity was increased from 2000 hr^{-1} to 3000 hr^{-1}. During the period 841 to 1058 hrs., the fresh feed space velocity was returned to 2000 hr^{-1} and the cold gas recycle ratio was increased from about 3:1 to about 9:1 to give a low deactivation rate of 0.0027 per cent/mscf/lb. When the cold recycle ratio was returned to about 3:1 in the period 1058 to 1760 hrs., the rate of cata-lyst deactivation was increased to 0.0187 per cent/mscf/lb. After 1760 hours, the unit was shut-down and put in standby condition under a hydrogen atmosphere. After the unit was restarted, the deactivation rate had increased greatly to 0.0821 per cent/mscf/lb., indicating that the increase in deactivation rate was associated with this particular shutdown. The fact that this experiment previously had under-gone three unscheduled shutdowns at 215, 798, and 894 hours with no adverse effect on performance, indicates that some unknown factor unique to the 1760 hour shutdown was responsible for the subsequent rapid decline in activity.

The operating data shown in table 5 were selected to provide more detailed in-formation on points of special interest in the experiment as follows:

Period 4...........represents performance at 2000 hr^{-1} fresh gas space velocity and 3:1 cold recycle when the catalyst is fresh.

Period 15..........represents performance at 2000 hr^{-1} space velocity before changes to 3000 hr^{-1}.

Periods 17 and 26...represent the beginning and end of the 3000 hr^{-1} space velocity operation.

Period 34..........represents operation at 2000 hr^{-1} space velocity and a high value of the cold gas recycle ratio (9.59:1).

Periods 37 and 62...represent the beginning and end of an operating period later in the experiment with 2000 hr^{-1} space velocity and 3:1 cold recycle ratio.

Periods 62 and 64...provide further comparison of the effect of increasing the cold recycle ratio from 3:1 to 10:1.

Period 76..........represents performance after a long period of operation, 2207 hours.

X-ray analysis of the spent catalyst (table 8) showed metallic nickel and nickel carbide, Ni_3C, in catalyst near the gas inlet and only metallic nickel in catalyst near the gas outlet.

DISCUSSION OF RESULTS

Operability

All four series of experiments have proven that the hot gas recycle methanation system is a usable and operable system. With a total gas recycle ratio of about 10:1 and with CO concentrations as high as 4.3 per cent (wet basis) in the mixed feed entering the catalyst bed, temperature control was excellent; no hot spots developed. It appears likely that lower recycle ratios, although it is not known how much lower, could be used successfully with an attendant increase in inlet CO concentration and an increase in temperature rise across the bed. Further testing is required to determine the limit in decreasing the total recycle ratio and the effect of such a decrease on the catalyst life.

Flame Sprayed Raney Nickel Plates vs Pellets of Precipated Catalyst in a Packed Bed

Results of experiment HGR-13 and HGR-14 have shown that the performance of the plates sprayed with Raney nickel catalyst was significantly better than that of the precipitated nickel catalyst pellets. The sprayed plates were better in that they yielded the higher production of methane per pound of catalyst, the longer catalyst life or lower rate of deactivation, the lower carbon monoxide concentration in the product gas, and the lower pressure drop across the catalyst bed.

One of the reasons for developing the parallel plate catalyst was to reduce the pressure drop across the catalyst bed and consequently reduce power costs for circulating the recycle gas. Pressure drop measurements across the 2 foot long catalyst beds are listed below:

Nominal Space Velocity, hr^{-1}		Pressure Drop , Inches Water	
Fresh Feed	Total Feed	Exp. HGR-14 (Parallel plates)	Exp. HGR-13 (1/4" pellets)
2000	22,000	2.0	28
3000	33,000	2.7	49

The above data show that the pressure drop across the parallel plates is in the order of $1/15^{th}$ that across the bed of pelleted catalyst.

The bed of parallel plates coated with Raney nickel catalyst was much more reactive than the bed of precipitated nickel. This was shown by the generally lower carbon monoxide concentration in the product gas during operation with the parallel plate bed; for example, after about 450 hours stream time, carbon monoxide in the product was 0.01 per cent for the bed of sprayed Raney nickel (HGR 14) and 0.05 per cent for the bed of precipitated nickel catalyst (HGR 13).

The higher reactivity of the plates coated with Raney nickel is further illustrated by the plots of catalyst temperature vs bed length shown in figure 10. The maximum bed temperature (indicating near completion of methanation) is consistently reached within a shorter distance from the gas inlet and the slope of the curves are correspondingly steeper for the more reactive bed of parallel plates coated with Raney nickel than for the bed of precipitated nickel.

The initial reactivities of the catalyst beds in experiments HGR-13 and 14 are considered to be satisfactorily high; however, the overall rate of deactivation of the bed of Raney nickel catalyst (0.029 per cent/mscf/lb) was much lower than that of the precipitated catalyst (0.076 per cent/mscf/lb). This, consequently, has resulted in a longer catalyst life (2307 vs 1368 hours) and a higher yield of methane per pound of catalyst (32.0 vs 11.5 mscf/lb) for the Raney nickel catalyst over that for the precipitated nickel catalyst.

Other precipitated nickel catalysts have been developed recently that reputedly are superior to that used in experiment HGR-13. These catalysts will be evaluated in the near future, as well as other forms of Raney nickel.

Effects of Cold Gas Recycle and Approach to Equilibrium

Product gases resulting from various cold recycle ratios are shown in table 9. For the experiments shown, a decrease in the cold recycle ratio resulted consistently in an increase in concentration in the product gas of water vapor, hydrogen, and carbon dioxide and a decrease in methane. These trends may be noted in experiment HGR-12 as the cold recycle ratio decreased from 8.7:1 to 1.2:1, in experiment HGR-13 as the cold recycle ratio increased from 1.0:1 to 9.1:1,and in experiment HGR-14 as the cold gas recycle · ratio decreased from 3.0:1 to 1.0:1. The above-mentioned trends indicate that the water gas shift reaction $CO + H_2O \rightarrow CO_2 + H_2$ was sustained to some degree. Except for the 462 hour period of experiment HGR-14, the apparent mass action constants for the water gas shift reaction based on the product gas compositions shown in table 9 remained fairly constant and ranged between 0.57 and 1.6. These values are much lower than the value of 11.7 for equilibrium conversion at 400° C. At 462 hours in experiment HGR-14, the apparent mass action constant for the shift reaction was 0.075, which represents a much greater departure from equilibrium than that encountered in the other periods shown in table 9. The apparent mass action constant for the methanation reaction $3H_2 + CO \rightarrow CH_4 + H_2O$ at 462 hours in experiment HGR-14 was 2650 which was a much closer approach to the 400° C equilibrium value of 1.7×10^4 than was achieved by the other test periods shown in table 9. This greater dominance by the methanation reaction while the catalyst is still relatively fresh probably caused the greater departure from equilibrium observed in the shift reaction during the early part of the experiment, at the 462 hour period.

Catalyst Deactivation

In this series of hot gas recycle experiments, the sulfur content in the feed gas was held very low, generally less than 0.1 ppm. Catalyst deactivation caused by sulfur poisoning is, therefore, considered negligible. On the other hand, the iron deposited on the catalyst in experiments HGR-10 and to a lesser extent in experiments HGR-12 and 14, is suspected of promoting carbon formation and subsequent fouling and deactivation of the catalyst. Iron concentrations of 5 mg/mscf have been determined in the recycle stream indicating the presence of iron carbonyl. Iron to nickel ratio in the fresh Raney nickel is about 2.4 Fe:1000 Ni, but the ratios are significantly higher for the spent Raney nickel catalyst. Based on analyses shown in table 8, Fe:Ni ratios for the spent Raney nickel catalysts of experiments HGR-12 and 14 ranged from 5.2 Fe:1000 Ni to 14.8 Fe:1000 Ni with the higher iron concentrations generally resulting in greater carbon deposition. The same trend was observed in experiment HGR-10.

Nickel carbide was detected on the catalyst in experiment HGR-14 and is another compound suspected of deactivating Raney nickel catalyst. However, inasmuch as the shutdown involved purging with hydrogen while the catalyst was hot, the presence of nickel carbide is contrary to Steffgen's (3) findings on a TGA apparatus that nickel

carbide is not stable under hydrogen at temperatures above 280° C. More information on nickel carbide formation is needed.

The metal surface area at the inlet end of the catalyst bed of experiment HGR-12 being smaller than at the outlet end indicates that a decrease in nickel metal sites is part of the deactivation process. Sintering of the nickel is one possible mechanism, but carbon and carbide formation are suspected major causes. The loss of active Raney nickel sites could also conceivably result from diffusion and subsequent alloying of residual free aluminum from unleached catalyst with the free nickel to form an inactive material.

As already noted in the experimental results of experiments HGR-12, 13, and 14, the ratio of catalyst deactivation increased as the fresh gas feed rate increased. It is possible that higher rates of carbon deposition and metal sintering occur at the higher feed rates to result in higher deactivation rates.

In comparing catalyst performance in an adiabatic hot gas recycle reactor vs an isothermal tube-wall reactor, the catalyst in the tube-wall reactor in experiment TWR-6 deactivated much slower than did the catalyst in the best gas recycle test, HGR-14, (0.009 vs 0.0291 per cent/mscf/lb) and produced much more methane per pound of catalyst (177 mscf/lb vs 32 mscf/lb). This indicates that adiabatic operation of a methanation catalyst between 300 and 400° C is not as efficient as operating isothermally at a higher temperature level of about 400° C.

Another factor that may account for the relatively higher rate of deactivation for the hot gas recycle reactor system is the entrainment of oil vapors from the hot recycle gas compressor into the catalyst bed. Evidence of this occurrence was shown by traces of heavy oil collected downstream of the hot gas recycle reactor. Such oil vapors would tend to decompose thermally and subsequently foul the catalyst surface with carbon. In future hot gas recycle tests, efforts will be made to eliminate the deposition of oil on the catalyst bed.

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TABLE 1. - Catalyst bed data from hot gas recycle reactor tests

Experiment Nos.	10	12	13	14
Type catalyst....................	Flame-sprayed Raney nickel	Flame-sprayed Raney nickel	Supported nickel	Flame-sprayed Raney nickel
Wt pct nickel....................	42 a/ b/	42 a/ b/	25	42
Pct activated...................	70	70	100% reduced	70
Plate thickness, ...inches	1/4	1/4	--	.046
Space between bare plates,-in.	.224	.224	--	.135
Av. bond coat thickness, inches	.006	.006	(1/4" x 1/4" cylindrical pellets)	.006
Av. catalyst thickness, inches	.026	.022		.022
Bed diameter x length, inches	3.07 x 60	3.07 x 60	3.07 x 24	3.07 x 24
Bed volume, ...ft³	.257	.257	.103	.103
Weight of unactivated catalyst.............lb	3.72	2.86	6.80	3.84
Superficial area of cat., ft²	12.7	12.7	18.6	11.4
Void fraction................	0.421	0.436	0.370	0.515

a/ Before leaching

b/ Leaching of aluminum stopped when 70% of the theoretical amount of hydrogen had evolved.

TABLE 2. - Operating data from selected periods in Experiment HGR-10

	5	15	26
Period number..................	5	15	26
Hours on stream	168	527	887
Fresh gas:			
Rate.................scfh	200	204	204
H_2 ....vol pct	75.3	75.3	75.6
CO ....vol pct	24.3	24.6	24.2
CO_2 ....vol pct	0.2	0.1	0.1
N_2 ....vol pct	0.0	0.0	0.0
CH_4 ....vol pct	0.2	0.1	0.2
H_2O ....vol pct	0.0	0.0	0.0
H_2/CO...................	3.10	3.06	3.09
Exposure vel........ scfh/ft2	15.7	16.0	16.1
Space vel......., hr^{-1}	779	795	796
Mixed feed gas (wet):			
Rate..............scfh	9138	3744	2401
H_2 ....vol pct	6.0	13.2	17.7
CO ....vol pct	1.2	2.9	4.3
CO_2 ....vol pct	1.3	0.7	0.8
N_2 ....vol pct	0.6	1.4	1.7
CH_4 ....vol pct	83.1	76.7	71.4
H_2O ....vol pct	7.8	5.0	4.1
H_2/CO	5.06	4.61	4.08
Inlet superficial vel.... f/s	5.44	2.18	1.44
Inlet Reynolds No.	5,000	1,960	1,180
Exposure vel........scfh/ft2	51.9	47.5	41.6
Space vel...........hr^{-1}	35,600	14,600	9,360
Vol. total recycle/vol. fresh gas	44.7	17.4	10.8
Vol. cold recycle/vol. fresh gas	3.1	2.99	3.05

continued:

TABLE 2. Operating data from selected periods in Experiment HGR-10

Period number...............	5	15	26
Temperatures:			
Gas inlet..............° C	370	355	375
Maximum catalyst........° C	400	425	475
Pressure...............psig	300	300	300
Product gas (wet):			
Rate................scfh	48.8	55.5	58.3
H_2..............vol pct	4.4	9.6	12.1
CO................vol pct	.7	1.6	2.4
CO_2............vol pct	1.3	.8	.2
N_2..............vol pct	.7	1.5	1.8
CH_4............vol pct	84.3	80.0	76.6
H_2O............vol pct	8.6	6.4	6.3
H_2/CO..............	6.2	6.0	5.05
Conversion:			
H_2........pct fresh feed	98.6	96.5	95.4
CO........pct fresh feed	99.3	98.2	97.2
$(H_2 + CO)$......pct fresh feed	98.7	96.9	95.9
H_2........pct mixed feed	27.0	29.9	34.6
CO........pct mixed feed	44.4	45.8	46.5
$(H_2 + CO)$......pct mixed feed	29.8	32.7	37.0
Usage ratio...............	3.07	3.01	3.07
Heating value ....Btu/scf	952	908	878
Carbon recovery...........pct	87	91	90

TABLE 3. – Operating data from selected periods in Experiment HGR-12

Period number.............	7	20	31	52	55	56
Hours on stream..........	200	539	803	1307	1379	1403
Fresh gas:						
Rate..................scfh	388	383	206	386	386	393
H_2...............vol pct	75.5	75.1	75.1	75.6	75.2	75.3
CO...............vol pct	24.4	24.7	24.7	24.4	24.7	24.6
CO_2.............vol pct	0.1	0.1	0.1	0	0.1	0
N_2..............vol pct	0	0	0	0	0	0
CH_4.............vol pct	0	0.1	0.1	0	0	0.1
H_2O.............vol pct	0	0	0	0	0	0
H_2/CO..............	3.09	3.04	3.04	3.10	3.04	3.06
Exposure vel.......scfh/ft^2	30.6	30.1	16.2	30.4	30.4	30.9
Space vel........hr^{-1}	1510	1490	804	1500	1500	1530
Mixed feed gas (wet):						
Rate..................scfh	7380	3450	5820	7760	9670	15,100
H_2...............vol pct	14.4	20.2	14.9	20.7	22.3	21.9
CO...............vol pct	2.0	4.2	1.6	4.4	4.2	3.8
CO_2.............vol pct	0.5	0.4	0.3	0.6	0.8	1.5
N_2..............vol pct	1.3	0.8	1.2	0.3	0.6	0.8
CH_4.............vol pct	76.4	70.7	76.6	72.6	66.8	60.8
H_2O.............vol pct	5.4	3.7	5.4	1.4	5.3	11.2
H_2/CO..............	7.04	4.82	9.20	4.71	5.34	5.70
Inlet superficial vel.......f/s	3.88	1.86	3.41	4.61	5.73	8.93
Inlet Reynolds No.	4,270	1,870	3,060	3,910	4,810	7,510
Exposure vel.......scfh/ft^2	95.6	66.3	75.8	153.0	201.0	306.0
Space vel........hr^{-1}	28,800	13,400	22,700	30,200	37,700	58,900
Vol. total recycle/vol. fresh gas	18.0	7.99	27.2	19.1	24.1	37.4
Vol. cold recycle/vol. fresh gas	3.01	2.99	3.04	8.71	3.01	1.20

continued:

TABLE 3. - Operating data from selected periods in Experiment HGR-12

Period Number		7	20	31	52	55	56
Temperatures:							
Gas inlet	°C	294	310	360	368	366	365
Maximum catalyst	°C	353	422	412	420	422	420
Pressure	Psig	300	300	300	300	300	300
Product gas (wet):							
Rate	scfh	94.6	97.6	45.9	98.8	105.5	127.7
H_2	vol pct	10.9	13.0	12.6	17.6	19.9	20.3
CO	vol pct	0.8	1.6	0.8	3.3	3.3	3.3
CO_2	vol pct	0.5	0.5	0.3	0.6	0.9	1.5
N_2	vol pct	1.3	0.8	1.2	0.3	0.6	0.8
CH_4	vol pct	79.7	77.5	78.8	75.6	69.0	62.2
H_2O	vol pct	6.8	6.6	6.3	2.6	6.3	11.9
H_2/CO		13.6	8.13	15.8	5.33	6.03	6.15
Conversion:							
H_2	pct fresh feed	96.5	95.6	96.3	94.0	92.8	91.2
CO	pct fresh feed	99.2	98.4	99.3	96.5	96.3	95.6
$(H_2 + CO)$	pct fresh feed	97.1	96.3	97.0	94.6	93.6	92.3
H_2	pct mixed feed	26.6	39.5	17.2	17.1	12.5	8.18
CO	pct mixed feed	62.3	64.4	53.6	26.6	22.8	16.0
$(H_2 + CO)$	pct mixed feed	31.1	43.8	20.7	18.7	14.1	9.34
Usage ratio		3.01	2.95	2.95	3.02	2.93	2.92
Heating value	Btu/scf	908	892	899	857	828	802
Carbon recovery	pct	80	81	72	83	81	87

TABLE 4. – Operating data from selected periods in Experiment HGR-13

Period number	6	20	22	34	37	50	54
Hours on stream	168	504	552	840	912	1224	1320
Fresh gas:							
Rate....scfh	211	216	310	320	211	205	210
H_2....vol pct	75.3	76.4	75.5	74.9	74.9	76.1	75.8
CO....vol pct	24.6	23.6	24.5	24.9	24.9	23.7	24.1
CO_2....vol pct	0	0	0	0.1	0.1	0.1	0.1
N_2....vol pct	0	0	0	0	0	0	0
CH_4....vol pct	0.1	0	0	0.1	0.1	0.1	0
H_2O....vol pct	0	0	0	0	0	0	0
H_2/CO	3.06	3.24	3.08	3.01	3.01	3.21	3.15
Exposure vel....scfh/ft2	11.3	11.6	16.7	17.2	11.3	11.0	11.3
Space vel....hr-1	2050	2110	3020	3120	2060	2000	2050
Mixed feed gas (wet):							
Rate....scfh	2260	2090	3400	3430	2040	2800	3010
H_2....vol pct	15.2	16.1	16.9	19.1	15.2	17.9	14.0
CO....vol pct	2.3	2.5	2.6	3.4	2.9	2.3	2.5
CO_2....vol pct	0.2	0.3	0.6	0.7	0.6	0.7	0.4
N_2....vol pct	0.9	1.4	1.0	0.9	0.9	0.5	1.2
CH_4....vol pct	76.9	75.6	74.5	71.9	76.7	66.8	81.0
H_2O....vol pct	4.5	4.1	4.4	4.0	3.7	11.8	0.9
H_2/CO	6.54	6.43	6.41	5.69	5.21	7.72	5.69
Inlet superficial vel....f/s	1.20	1.11	1.81	1.82	1.09	1.49	1.60
Inlet Reynolds No.	835	772	1240	1220	753	1010	1120
Exposure vel....scfh/ft2	21.3	21.0	35.8	41.5	19.9	30.5	26.6
Space vel....hr-1	22,000	20,400	33,100	33,400	19,900	27,300	29,400
Vol. total recycle/vol. fresh gas	9.73	8.68	9.98	9.73	8.68	12.7	13.3
Vol. cold recycle/vol. fresh gas	2.98	2.99	3.00	2.96	2.98	1.01	9.05

continued:

TABLE 4. - Operating data from selected periods in Experiment HGR-13

Period number		6	20	22	34	37	50	54
Temperatures:								
Gas inlet	°C	301	300	301	301	302	301	301
Maximum catalyst	°C	401	400	401	400	401	401	400
Pressure	psig	300	300	300	300	300	300	300
Product gas (wet):								
Rate	scfh	48.1	50.9	79.3	81.1	49.0	47.4	38.4
H_2	vol pct	8.8	9.0	10.8	13.1	8.2	13.1	9.2
CO	vol pct	0	0.1	0.4	1.1	0.4	0.6	0.8
CO_2	vol pct	0.3	0.3	0.7	0.8	0.6	0.8	0.4
N_2	vol pct	0.9	1.5	1.0	0.9	1.0	0.5	1.3
CH_4	vol pct	83.0	82.2	80.3	77.8	83.6	71.0	85.7
H_2O	vol pct	7.0	6.9	6.8	6.3	6.2	14.0	2.6
H_2/CO		-	90	27	11.9	20.5	21.8	11.5
Conversion:								
H_2	pct fresh feed	97.3	97.2	96.3	95.6	97.5	96.0	97.8
CO	pct fresh feed	100	99.9	99.6	98.9	99.6	99.4	99.4
$(H_2 + CO)$	pct fresh feed	98.0	97.9	97.1	96.4	98.0	96.8	98.2
H_2	pct mixed feed	45.0	47.2	39.1	34.9	49.6	29.9	37.0
CO	pct mixed feed	100	96.2	85.3	68.2	87.9	74.4	68.0
$(H_2 + CO)$	pct mixed feed	52.3	53.8	45.3	39.8	55.7	35.0	41.6
Usage ratio		2.71	2.95	2.73	2.91	2.94	3.10	3.09
Heating value	Btu/scf	935	926	911	890	933	888	925
Carbon recovery	pct	82	87	90	80	78	70	63

TABLE 5. - Experiment HGR.14 - Selected Test Data

	4	15	17	26	34	37	62	64	76
Period number..............	4	15	17	26	34	37	62	64	76
Hours on stream............	139	462	534	750	1058	1130	1732	1803	2091
Fresh Gas:									
Rate.............scfh	207	214	306	307	207	207	210	203.5	213
H_2.............vol pct	75.8	75.4	75.3	74.6	75.1	75.4	75.1	74.7	75.4
CO.............vol pct	23.7	23.6	23.6	24.4	22.9	23.6	24.0	24.8	24.1
CO_2.............vol pct	0.1	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.1
N_2.............vol pct	0.4	0.9	0.7	0.8	1.8	0.8	0.8	0.3	0.4
CH_4.............vol pct	0	0	0.1	0	0.1	0.1	0	0.1	0
H_2O.............vol pct	0	0	0	0	0	0	0	0	0
H_2/CO..........	3.20	3.19	3.19	3.06	3.28	3.19	3.13	3.01	3.13
Exposure vel......scfh/ft^2	18.0	18.6	26.5	26.6	17.8	17.9	18.2	17.7	18.6
Space vel......hr^{-1}	2010	2090	2980	2990	2020	2020	2050	1980	2080
Mixed feed gas (wet):									
Rate.............scfh	2360	2400	3710	3720	2240	2430	2760	2120	2430
H_2.............vol pct	15.9	14.0	11.7	8.8	11.8	11.1	10.1	10.4	13.8
CO.............vol pct	2.1	2.1	2.0	2.2	2.2	2.2	2.1	2.9	2.9
CO_2.............vol pct	0.1	0.1	0.2	1.5	0.2	0.4	0.7	0.4	0.7
N_2.............vol pct	0.7	1.1	0.9	1.1	1.3	0.9	1.1	1.1	1.2
CH_4.............vol pct	76.4	78.0	80.6	81.9	84.3	80.7	81.4	85.2	76.9
H_2O.............vol pct	4.8	4.6	4.6	4.5	0.2	4.7	4.6	0	4.5
H_2/CO..........	7.68	6.63	5.88	4.00	5.38	5.10	4.84	3.64	4.77
Inlet superficial vel...f/s	1.25	1.27	1.97	1.97	1.19	1.29	1.46	1.12	1.29
Inlet Reynolds No........	546	563	882	898	532	582	666	512	570
Exposure vel......scfh/ft^2	37.2	34.0	44.5	35.8	27.5	28.2	29.6	24.8	35.6
Space vel......hr^{-1}	23,000	23,400	36,100	36,200	21,800	23,700	26,900	20,700	23,700
Vol. total recycle/vol.fresh gas	10.7	10.4	11.3	11.3	10.1	11.0	12.4	9.66	10.6
Vol. cold recycle/vol.fresh gas	2.95	2.93	3.12	3.01	9.59	2.93	3.13	10.2	2.94

continued:

TABLE 5. - Experiment HGR 14 - Selected Test Data

Period number	4	15	17	26	34	37	62	64	76
Temperatures:									
Gas inlet...°C	299	299	301	300	300	300	300	299	299
Maximum catalyst...°C	400	400	400	400	401	400	395	397	398
Pressure...psig	300	300	300	300	300	300	300	300	300
Product gas (wet):									
Rate...scfh	32.9	28.4	44.2	45.4	27.3	27.6	43.9	44.7	40.6
H₂...vol pct	10.0	7.9	5.8	2.8	5.3	5.0	4.7	3.5	7.8
CO...vol pct	0	0	0.1	0.2	0.1	0.2	0.3	0.5	0.9
CO₂...vol pct	0.1	0.1	0.2	1.6	0.2	0.5	0.7	0.5	0.7
N₂...vol pct	0.7	1.1	0.9	1.1	1.2	0.9	1.1	1.2	1.3
CH₄...vol pct	81.9	83.9	86.1	87.6	90.7	86.3	86.5	91.8	82.5
H₂O...vol pct	7.3	7.0	6.9	6.7	2.5	7.1	6.7	2.5	6.8
H₂/CO	-	785	117	14.1	58.3	27.7	16.2	6.68	9.14
Conversion:									
H₂...pct fresh feed	97.9	98.6	98.9	99.4	99.1	99.1	98.7	99.0	97.9
CO...pct fresh feed	100	100	100	99.9	99.9	99.9	99.7	99.5	99.2
(H₂ + CO)...pct fresh feed	98.4	98.9	99.1	99.5	99.3	99.3	98.9	99.1	98.2
H₂...pct mixed feed	40.4	47.0	52.2	69.5	57.7	57.0	55.4	67.8	46.5
CO...pct mixed feed	100	99.6	97.8	91.5	96.2	92.2	86.8	82.6	72.1
(H₂ + CO)...pct mixed feed	47.3	53.9	58.9	73.9	63.7	62.7	60.8	71.0	50.9
Usage ratio	3.10	3.13	3.14	3.04	3.23	3.15	3.09	2.99	3.08
Heating value...Btu/scf	930	941	957	962	961	960	956	967	927
Carbon recovery...pct	83.1	74.2	79.0	78.5	94.5	98.3	94.4	89.4	86.5

TABLE 6.   IRON AND CARBON CONTENT OF RANEY NICKEL CATALYST GRIDS

AFTER EXPERIMENT HGR-10

GRID	Weight Percent Fe	Weight Percent C
A[1]	22.0	13.4
B	17.2	9.1
C	3.5	3.9
D	2.7	3.3
E	2.0	2.5
F	2.1	2.0
G	.9	1.5
H	.8	1.6
I	.8	1.6
TOP[2]	.8	1.9

[1] GAS IN
[2] GAS OUT

TABLE 7. SURFACE AREAS, PORE VOLUMES, AND PORE RADII

OF SPENT RANEY NICKEL CATALYST

EXPERIMENT HGR-12

DISTANCE FROM GAS INLET, INCHES	B.E.T. SURFACE AREA, m^2/gm	AV. PORE RADIUS, $\overset{\circ}{A}$	PORE VOL. cm^3	PERCENT PORE VOLUME WITH THE FOLLOWING RADII				
				$< 30\overset{\circ}{A}$	$30-40\overset{\circ}{A}$	$40-50\overset{\circ}{A}$	$50-60\overset{\circ}{A}$	$>60\overset{\circ}{A}$
0	34.7	47.1	0.083	19.7	11.9	10.8	10.0	47.6
18	31.7	90.6	.146	8.8	6.2	4.9	6.4	73.6
30	34.4	58.6	.101	15.7	9.2	11.6	9.5	54.0
36	32.9	82.0	.135	10.4	7.4	8.0	6.0	68.2
48	24.2	139.0	.168	.5	3.7	7.5	4.7	83.6
60	19.5	109.5	.107	0	0	0	4	96.0

TABLE 8. - Properties of spent methanation catalysts

	Exp. HGR-12 Catalyst		Exp. HGR-13 Catalyst		Exp. HGR-14 Catalyst	
	At Inlet	At Outlet	At Inlet	At Outlet	At Inlet	At Outlet
X-Ray analysis	-	-	Ni	Ni	Ni, Ni3C	Ni
Chemical analysis, per cent:						
Ni	67.6	80.4	24.0	25.3	83.4	81.9
Al	13.1	9.6	-	-	6.23	7.90
C	1.74	0.8	5.1	5.2	3.53	0.81
Fe	0.35	0.45	0.12	0.20	1.18	1.21
Na	0.08	0.06	0.23	0.20	-	-
S	0.24	0.13	0.1	0.1	0.19	0.07
Surface area (B.E.T.), m^2/gm	34.67	19.50	-	-	30.95	29.7
Metal surface area (chemisorbed hydrogen), m^2/gm	1.3	4.9	-	-	-	-
Average pore radius, Å	47.07	109.53	-	-	48.01	56.69
Percent pore volume > 60Å	47.56	95.97	-	-	42.3	64.2

TABLE 9. - Effect of cold recycle upon product gas

Exp. No.	Stream time, hours	Cold recycle ratio	H_2O in mixed feed, %	Product gas analysis, per cent, wet basis					Apparent mass action constants, k_p		Max temp, °C
				H_2O	H_2	CO	CO_2	CH_4	shift reaction	methanation reaction	
HGR-12	1307	8.7:1	1.4	2.6	17.6	3.3	0.6	75.6	.78	.24	420
HGR-12	1379	3.0:1	5.3	6.3	19.9	3.3	0.9	69.0	.86	.37	422
HGR-12	1403	1.2:1	11.2	11.9	20.3	3.3	1.5	62.2	1.2	.59	420
HGR-12	539	3.0:1	5.4	6.6	13.0	1.6	0.5	77.5	1.6	3.2	422
HGR-13	1224	1.0:1	11.8	14.0	13.1	0.6	0.8	71.0	.79	16.0	401
HGR-13	1320	9.1:1	0.9	2.6	9.2	0.8	0.4	85.7	.57	7.8	400
HGR-14	462	2.9:1	4.6	7.0	7.9	0.01	0.1	83.9	.075	2650	400
HGR-14	2091	3.0:1	4.5	6.8	7.8	0.9	0.7	82.5	1.02	30.8	398
HGR-14	2307	1.0:1	10.5	13.2	10.1	0.8	1.4	73.0	.75	25.3	398
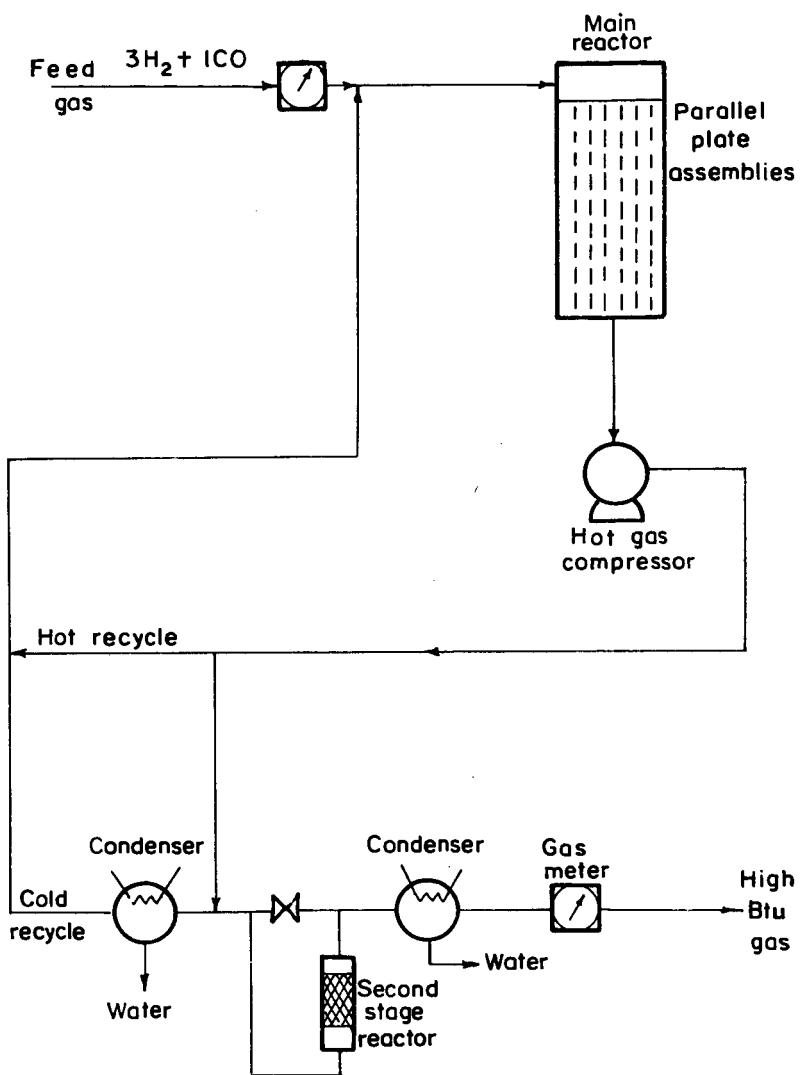
Figure 1 — Flowsheet of hot-gas recycle process

L-13681
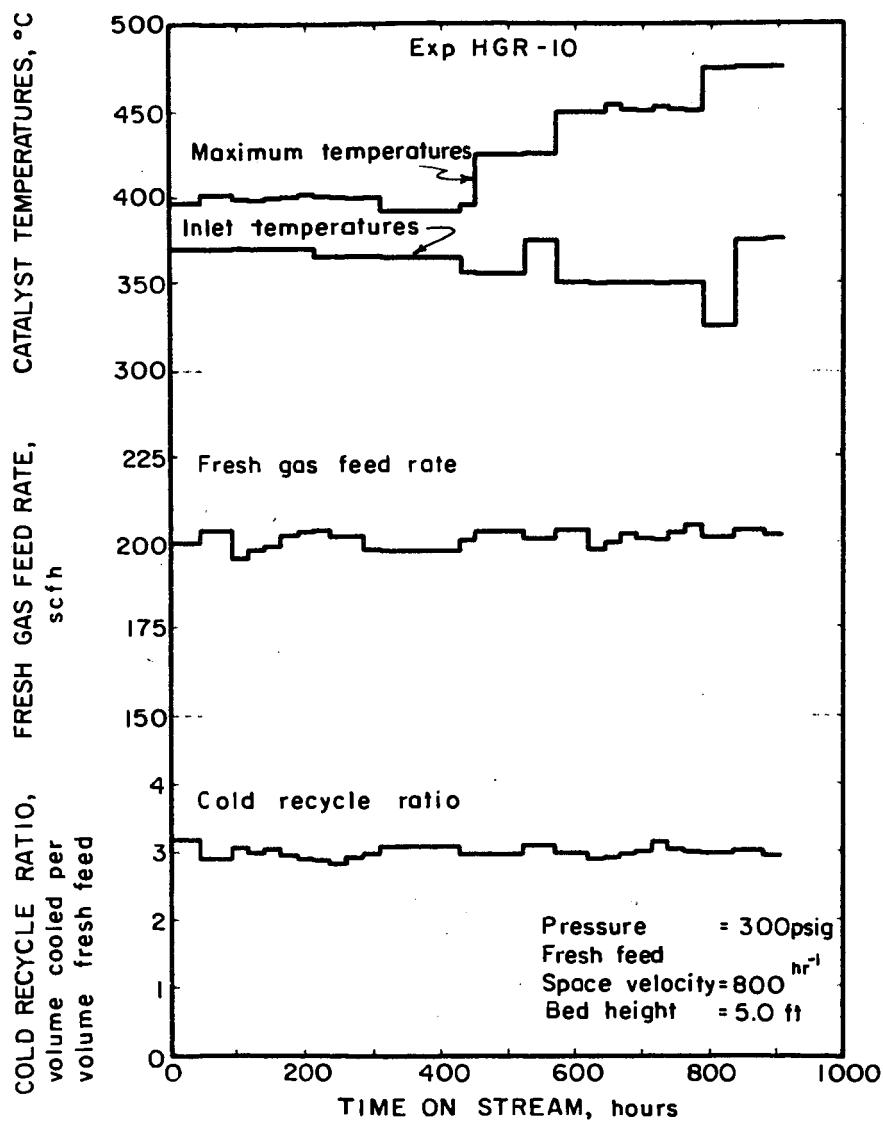
Figure 2 — Reactor conditions.

L-13676
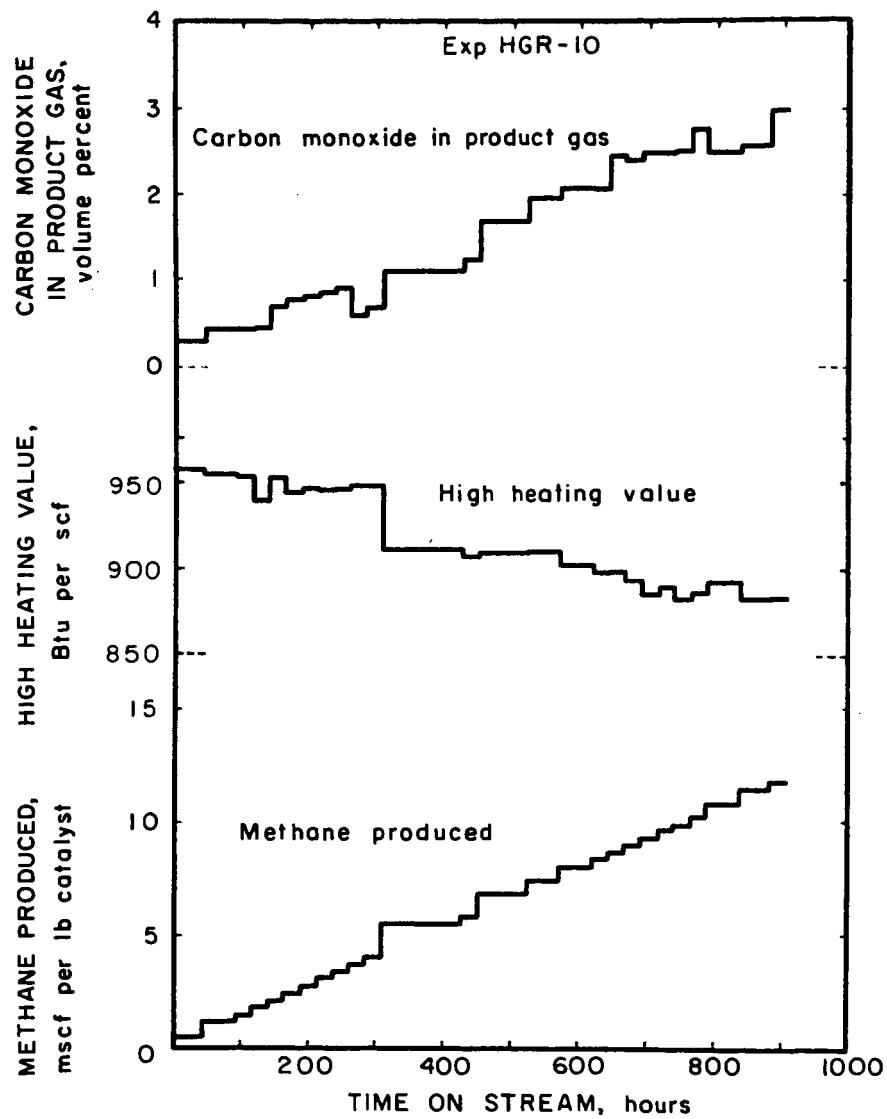
Figure 3 — Product gas characteristics

L-13673
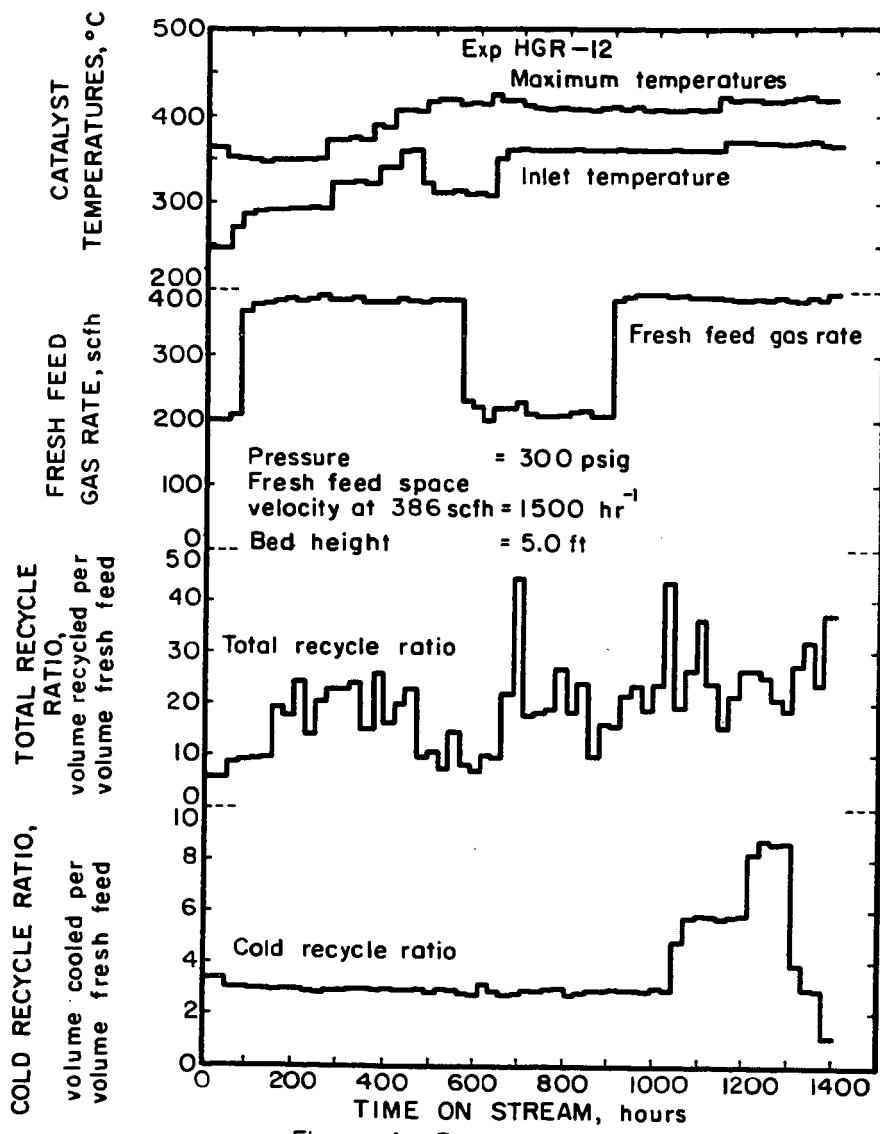
Figure 4 — Reactor conditions

L-13678
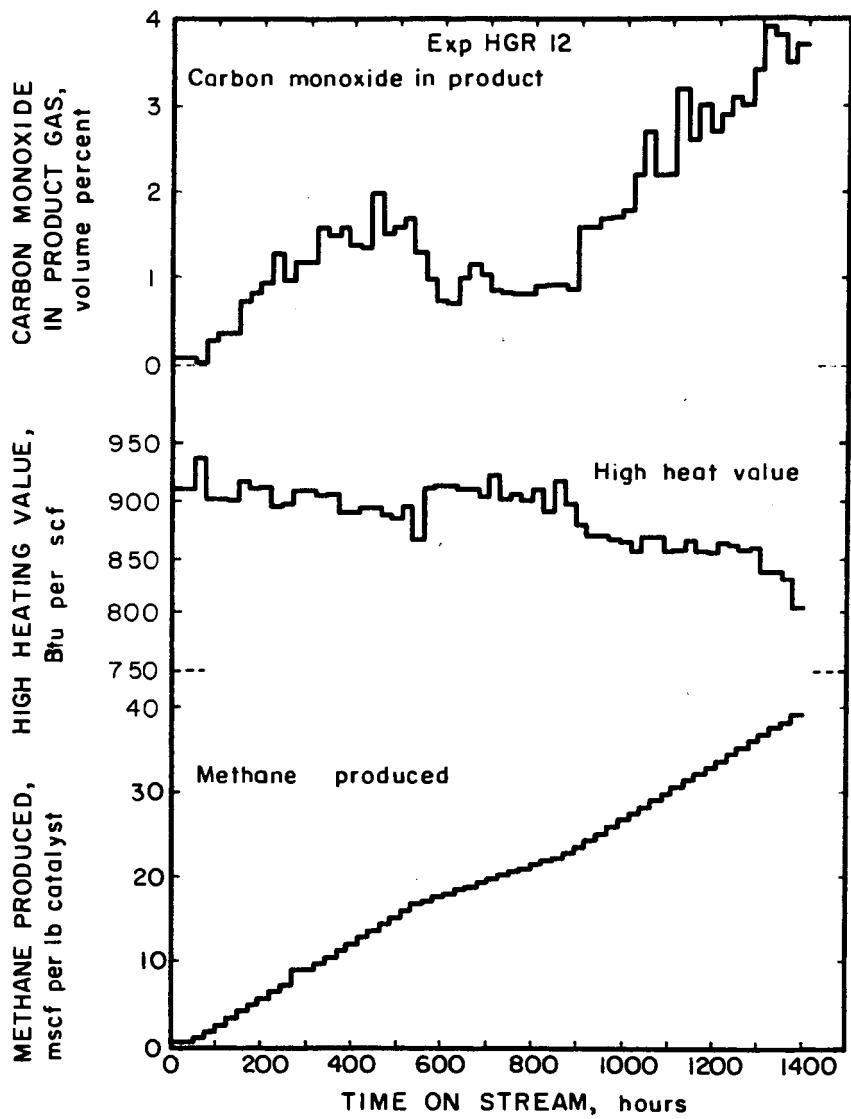
Figure 5 – Product gas characteristics

L-13674
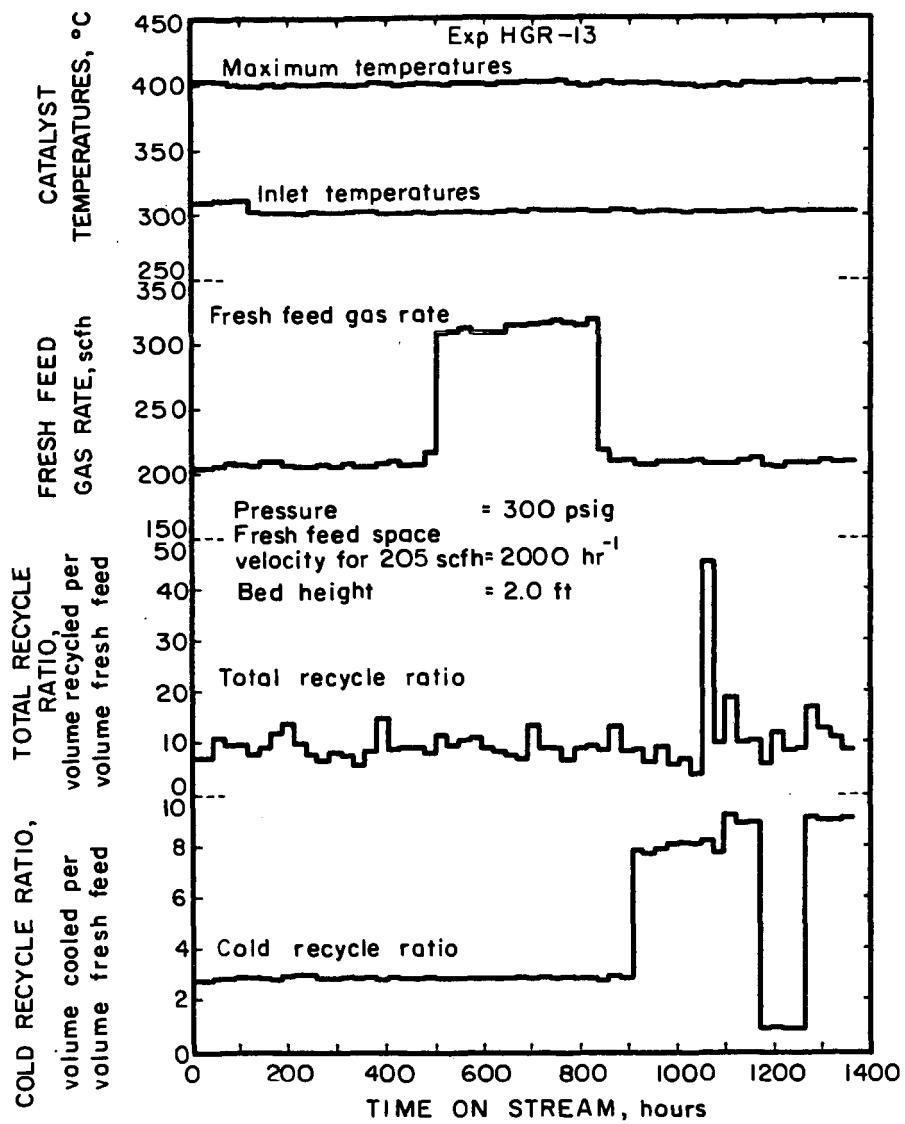
Figure 6 — Reactor conditions

L-13677
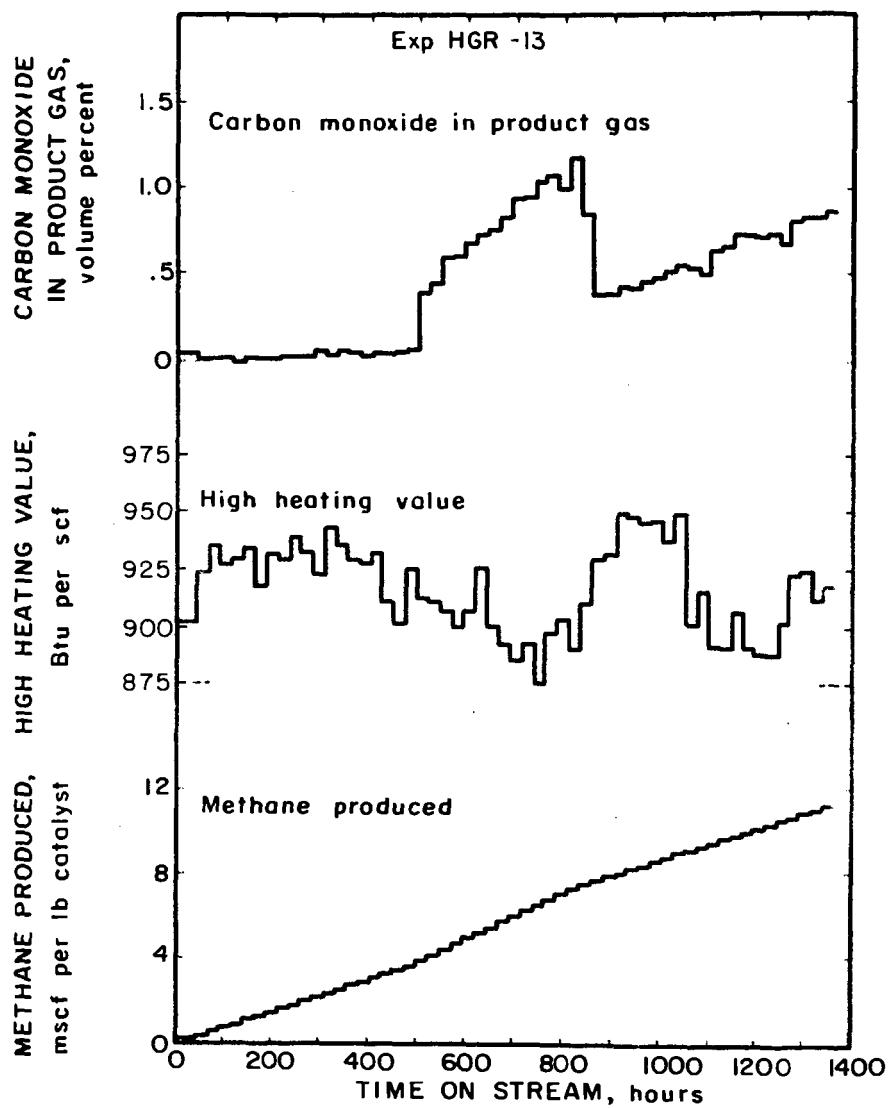
Figure 7 — Product gas characteristics

L-13675
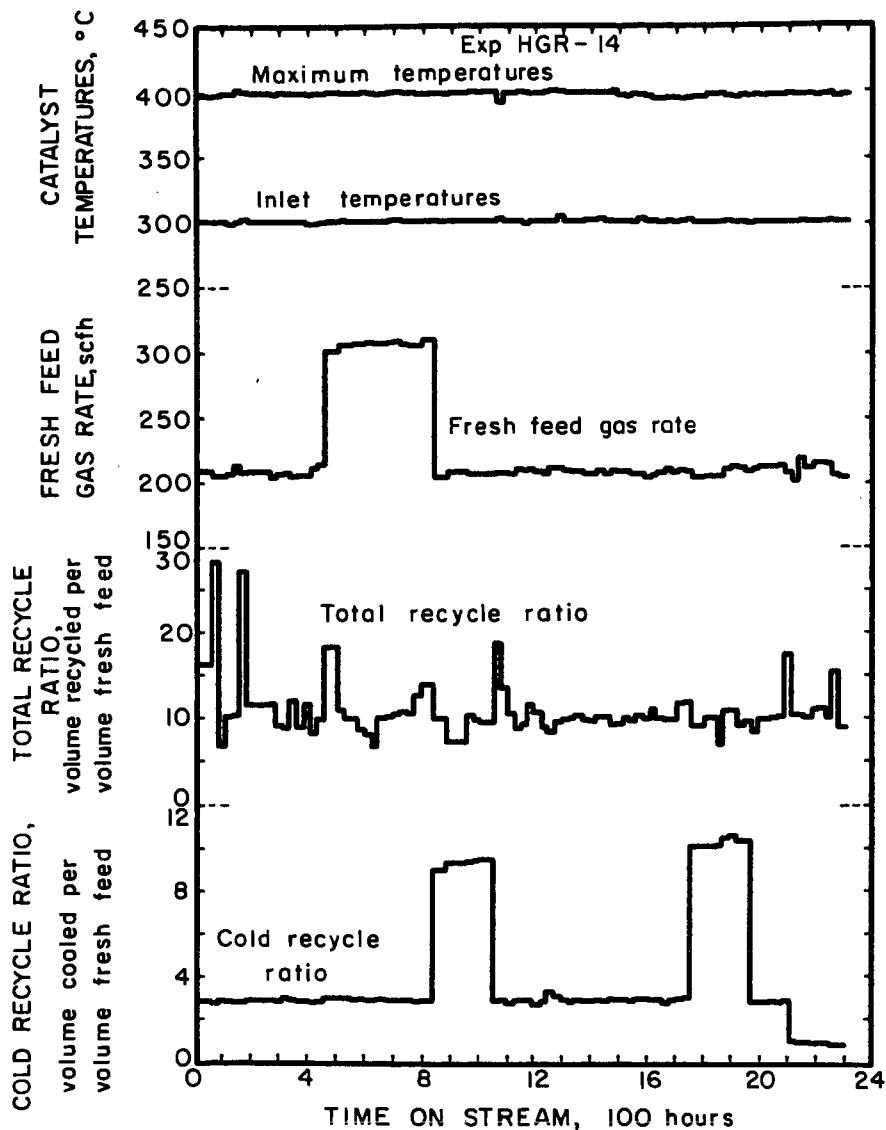
Figure 8 — Reactor conditions

L-13680
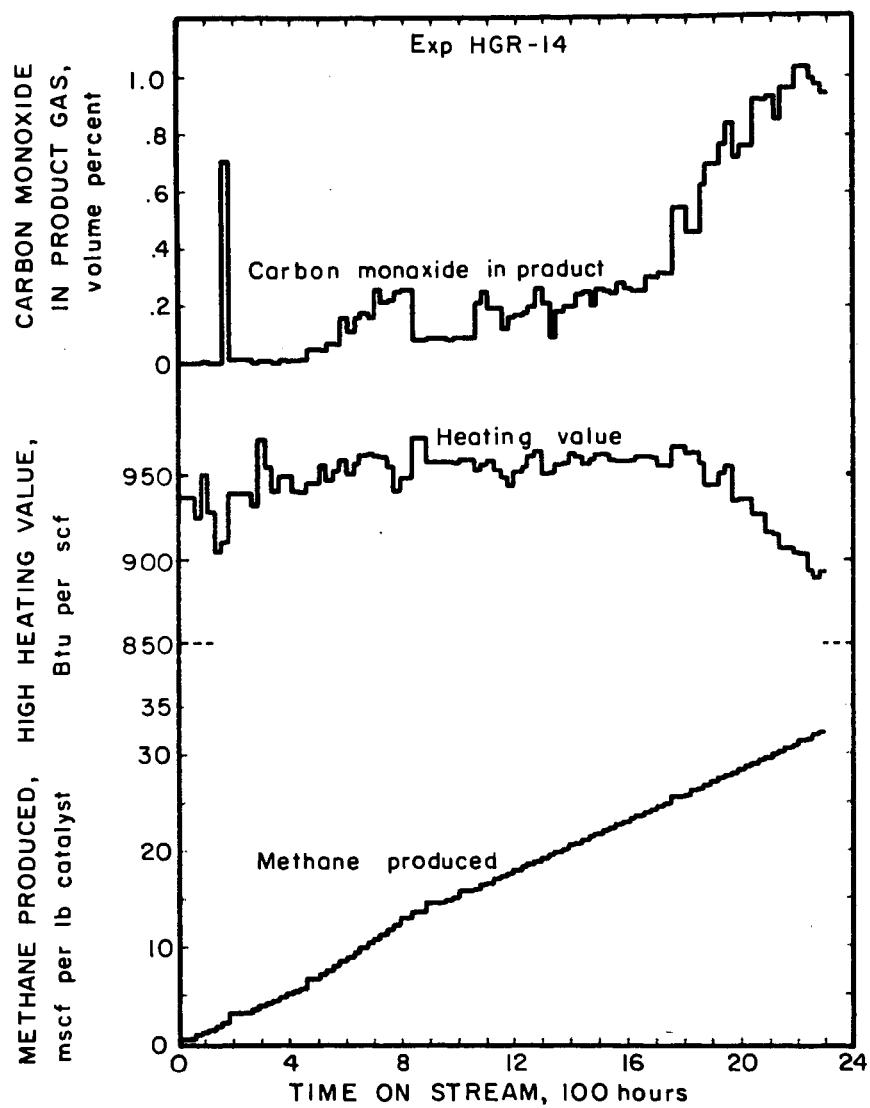
Figure 9— Product gas characteristics

L-13679
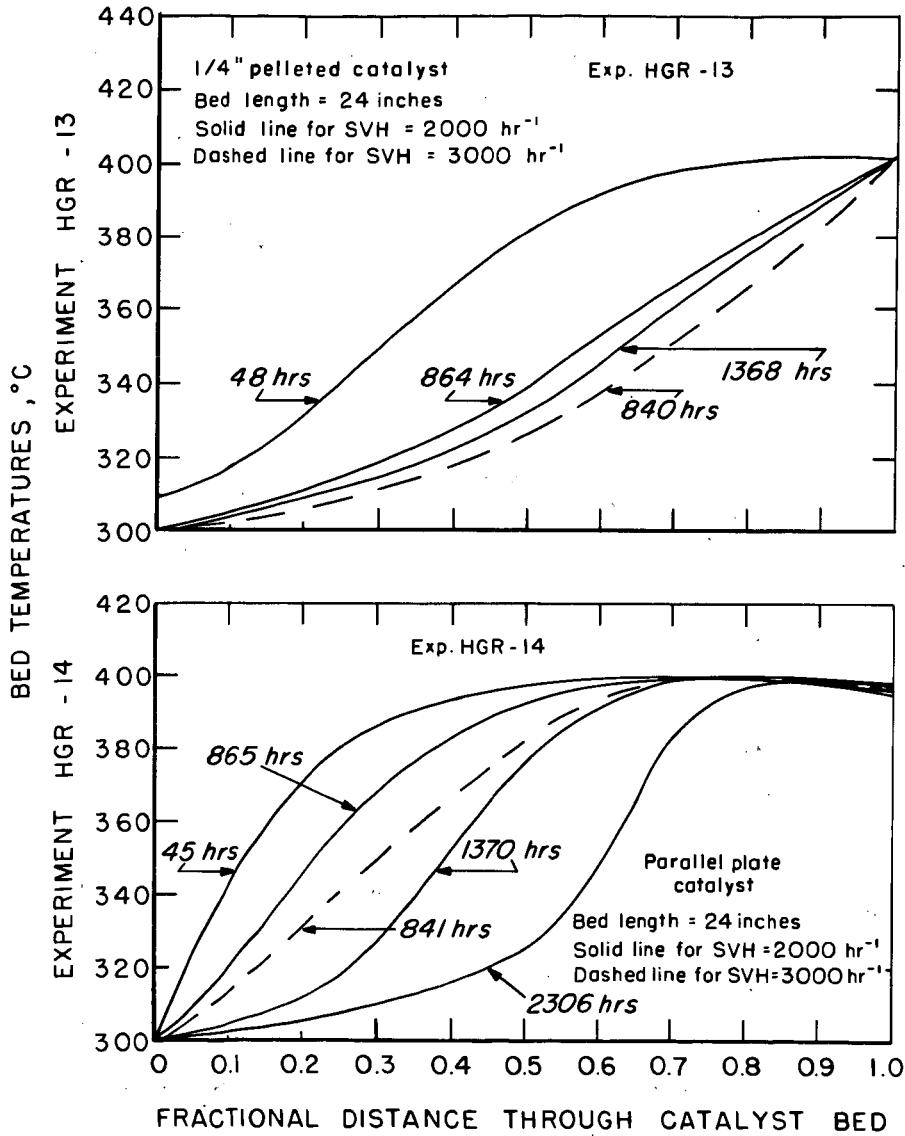
FIGURE 10-Axial temperature profiles, methanation Exp. HGR 13 and 14.

L-13752