HYGAS: 1964 TO 1972. PIPELINE GAS FROM COAL--HYDROGENATION (IGT HYDROGASIFICATION PROCESS). VOLUME 3

INSTITUTE OF GAS TECHNOLOGY, CHICAGO, ILL

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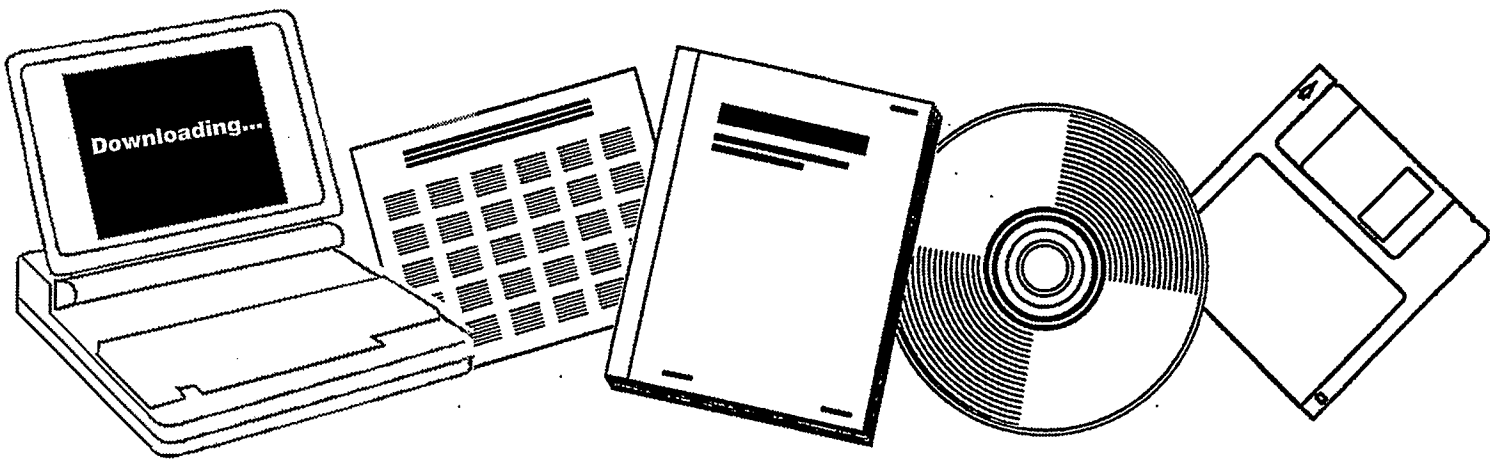

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PIPELINE GAS FROM COAL — HYDROGENATION
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Final Report

by

IGT Process Research Division

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July 1975

PART V

METHANATION

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5.0. Summary of Methanation

In this section, the work carried out on the evaluation of catalysts for the methanation of coal gasification effluent gas streams (to raise the heating value to the level of pipeline gas) is reported. Both the conventional packed-bed reactor (PBR) and a continuous-stirred-tank reactor (CSTR) used in the study, along with the associated instrumentation, are described. The "perfect-mixing" zone for the CSTR is established experimentally. Operation in the "perfect-mixing" zone in the CSTR eliminates the temperature and concentration gradients, and permits an easier evaluation of the kinetics of a chemical reaction.

A nine-step test program was developed to evaluate various catalysts on the same basis. Since 1964, a total of 37 commercially available and newly developed catalysts have been tested. Not all the catalysts were subjected to the complete test program; evaluation was stopped at the step where a catalyst failed. Performance data for each catalyst tested are available, if not reported herein.

The catalyst properties evaluated were activity, physical strength, upper and lower temperature limits, resistance to poison, selectivity for methanation reaction and the life performance. No single catalyst satisfies all the requirements of an ideal catalyst. For example, some activity may have to be sacrificed for additional physical strength, or the lower temperature limit may have to be raised for satisfactory operation at higher temperatures. However, the new generation of catalysts developed specifically for the methanation of coal gasifier effluents are overcoming the earlier deficiencies of the older commercially available catalysts.

For most of the catalysts studied, the hydrogen-to-carbon monoxide ratio in the feed gas should not be less than 2.85 for the temperatures between 525° and 900°F and for pressures above 600 psig. The catalysts that were deactivated by an even lower H_2:CO ratio and/or undesirable temperatures could not be regenerated.

The presence of large amounts of methane in the feed gas has a small effect on the rate of methanation as long as the relative partial pressure of methane is low, as compared to that of hydrogen. More studies are required in this area, especially for low-pressure coal gasification processes.

The presence of 1 mole percent (or less) benzene does not affect the methanation catalysts. The presence of higher concentrations of benzene tends to reduce methanation activity gradually and in steps. Furthermore, the methanator temperature must not be allowed to increase uncontrollably while benzene is present; otherwise, carbon will be deposited. Most of the catalysts were not regenerable after benzene deactivation.

If both CO and CO_2 are present in the feed, CO_2 will be hydrogenated to methane only when the concentration of CO is less than 0.2 mole percent. Excess CO_2 (15 percent or more) may hinder the CO methanation reaction.

The presence of nitrogen in the coal gasifier effluent (methanator feed) may cause ammonia formation because nickel and iron in the catalyst (or in the

reactor walls) promotes ammonia formation in the absence of carbon oxides. Ammonia tends to deactivate the methanation catalyst, but it can be regenerated by passing hydrogen at about 700°F. However, carbon deposition usually follows deactivation.

The effect of sulfur on the catalyst activity was determined in life-test type runs. Generally, small concentrations (< 1 ppm) of propyl mercaptan and thiophene do not affect the nickel catalysts. However, methyl mercaptan, carbonyl sulfide and hydrogen sulfide in excess of 1.2 ppm quickly poison the nickel catalysts. Carbon deposition took place after deactivation. Neither the sulfided catalysts nor the carbon deposited catalysts were regenerable.

Life testing results of three promising catalysts are summarized.

5.1 Introduction

The existing coal gasification processes produce a reactor output gas (prior to clean-up and methanation) with a heating value of from 300 to 600 Btu/SCF per standard cubic foot; this consists primarily of methane, hydrogen and carbon oxides. In order to produce a gas with a heating value of about 1000 Btu per standard cubic foot, and that is interchangeable with pipeline gas, methanation of the above-mentioned gas is essential. Heterogeneous catalysis — the heart of the methanation process — is by nature difficult and inconsistent, because:

- First there is no guarantee that two batches of catalysts will be made exactly alike.

- Second there is no guarantee that the molecules which meet the catalyst will have the same number and the same composition at all times.

The critical aspects of the methanation process are catalyst performance and the removal of exothermic heat of reaction. Since 1952 HYGAS researchers have used fixed-bed and fluidized-bed catalytic reactors to determine the most promising combination of catalyst performance and reactor design. Since 1964 this work has intensively evaluated catalyst performance. As this is written in mid-1974 HYGAS researchers have evaluated 37 commercially available and newly developed catalysts (Table 5-1). Although not all the catalysts in Table 5-1 were subjected to the extensive test program described below, the total performance data for each catalyst are listed.

The test program employed in these catalyst evaluations is as follows:

Step 1: The activity of the catalyst is determined at temperature, T_1, Pressure, P_1, flow rate, Q_1, and at feed composition, X_1, simulating purified coal gasifier effluent. These data provide the base line for comparison with any other catalyst as well as for sequential-test comparisons of the subject catalyst.

Step 2: The upper temperature limit is determined. The reactor temperature is increased gradually and continuously until the temperature is

Table 5-1. CATALYSTS TESTED TO DATE

Catalyst	Tested for Steps Listed								
	1	2	3	4	5	6	7	8	9
CCI 13-3, 1/4 x 1/4 in.	●	●	●			●			
CCI 13-4, 1/8-in. extrusions	●	●	●	●		●			
CCI 13-4, 3/16 to 5/16 in. spheres	●	●	●						
CCI X C150	●	●							
CCIC-150-4-03	●								
G-3B, 1/4 x 1/4 in.	●								
G-65, 1/4 x 1/4 in.	●	●	●	●		●	●	●	●
G-41	●								
G-74, 3/16 x 3/16 in.	●								
G-87*	●	●	●						
T-309B, 1/8 x 1/8 in.	●	●							
T-311, 3/16 x 1/8 in.	●								
T-311, 1/8 x 1/8 in.	●	●	●						
T-1183, 3/16 x 3/16 in.	●								
UC 8, 1/8-in. spheres	●	●	●	●					
UC 204-41, 1/8-in. extrusions	●	●	●	●		●	●		
UC 344-9, 1/16-in. extrusions	●			●		●	●	●	
UC 466-34, 1/16-in. extrusions	●	●	●	●		●			
UC 681-74, 1/8-in. extrusions	●								●
UC 964-34*	●	●	●	●					●
Meta-2	●	●	●	●					
Katalco 7-2	●								
Katalco 15-5	●								
SaSol E-5637	●								
Ammonia Synthesis Catalyst	●	●							
Lathe Turnings	●	●		●					
Ni-0116T, 1/8 x 1/8 in.	●								
Ni-0101T, 1/4 x 1/4 in.	●	●	●	●	●				
Ni-0104T, 1/4 x 1/4 in.	●	●	●	●	●	●	●	●	●
Ni-X-321A-36-3-8	●								
Ni-4303E, 1/12 in.	●	●							
CoMo-0601T, 1/8 x 1/8 in.	●		●	●					
HT-100E, 1/16 in.	●	●							
Eng. 12468 1/8 in. (Ru)	●	●	●	●			●		
Eng. 13958 1/8 in. (Pt)	●		●						
Eng. 11933 1/8 in. (Ph)	●		●						
Eng. 13391 1/8 in. (Pd)	●		●						
Mallinckrodt 21A-191A*									
LDI-X825*									

*Being evaluated

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reached where the catalyst performance is not acceptable. The temperature then is returned to T_1 while other conditions remain the same and the activity is measured again. This activity is compared with that obtained in Step 1. If the activity remains the same, the upper temperature limit is established; if the activity decreases, the reactor is reloaded with a fresh batch of the same catalyst and tested at a temperature slightly below that reached in the earlier test. After the activity is measured, the temperature is again reduced to T_1, and the activity is compared with that obtained in Step 1. This procedure is repeated until the upper temperature limit of the candidate catalyst is established.

Step 3: The lower temperature limit is determined. The procedure is the same as that used for Step 2, except that the temperature is decreased instead of increased.

Step 4: The thermal resistance of the catalyst is determined at its upper temperature limit. Two tests are involved.

First, the catalyst is held in a hydrogen atmosphere at its upper temperature limit for about three days. The temperature then is to be dropped to T_1. Other conditions are set at P_1, Q_1, and X_1, and the activity of the catalyst is measured and compared with that in Step 1.

Second, the activity of the catalyst is measured at its upper temperature limit with other conditions at P_1, Q_1 and X_1 for three days, then dropped to T_1 and measured again and compared to that of Step 1. These steps are repeated until the thermal resistance level is established. Fresh catalyst is used for each test and Step 1 is repeated at the beginning of each test to confirm that the catalyst used has the same original performance.

Step 5 The effect of C_6H_6, NH_3, or any other potential catalyst poison that may be contained in the feed gas to methantor is investigated.

Step 6: The effects of pressure on the reaction rate are studied. At least three pressures are investigated. The activity of the catalyst as well as its upper and lower temperature limits are determined for each pressure. The test procedure is essentially the same as that outlined in Steps 1, 2, and 3, but may not be as detailed as that in the previous investigations.

Step 7: The kinetics (the effect of temperature on reaction rate) are studied. At least three temperatures within the temperature limits determined in Steps 2 and 3 are studied. During this study, the feed composition X_1 is also varied because the rate of reaction is a function of temperature, pressure, and the composition. The approach is as follows:

a) Feed gas containing H_2, CO is used for the entire temperature and pressure range for each qualified catalyst. By varying the concentration of CO, the order with respect to CO is determined.

b) Feed gas containing H_2, CO, and He is used. By keeping the CO concentration constant at several levels and varying that of the H_2 while using He as the balance gas, the order with respect to H_2 is determined.

c) Feed gas containing H_2, CO, and CH_4 (in place of He) is used for the same conditions as in Step 7b. The order with respect to CH_4 is determined.

d) Feed gas containing H_2, CO, CH_4, and CO_2 is used. The order with respect to CO_2 is determined.

e) Feed gas containing H_2, CO, CH_4, and H_2O is used. The order with respect to H_2O is determined.

f) Feed gas containing H_2, CO, CH_4, CO_2, H_2O and C_6H_6 is used. The order with respect to C_6H_6 is determined.

g) Feed gas containing H_2, CO, CH_4, CO_2, H_2O, C_6H_6 and N_2 is used. The order with respect to N_2 is determined.

Step 8: Trace quantities of sulfur compounds such as C_2H_5SH, C_4H_4S, and COS are tested to determine their effect on the catalyst activity. The effect of H_2S is determined only if the catalyst manufacturer claims that the catalyst is sulfur resistant.

Step 9: If the catalyst passes the tests mentioned above, a life test of 1000 hours or more is conducted. During this test, the temperature of the reactor is cycled between the predetermined temperature limits. The pressure is held at what would be coal gasification plant pressure. The space velocity is increased to the CO breakthrough point. Steam is added in various quantities to the feed gas from time to time, and the feed composition is changed from a composition of a recycled gas to its original feed composition. Experimental work continues 24 hours a day over the entire test period. Data are collected during two of the three daily shifts. The third shift is unattended; during this shift test equipment is operated automatically at steady-state conditions.

Steps 5, 6, 8 and 9 are performed in a packed-bed reactor (PBR). Test steps 1, 2, 3, 4 and 7 are performed in a continuous-stirred-tank-reactor (CSTR).

5.2 Apparatus

Two types of reactors were selected for this study. One is the conventional packed bed reactor (PBR) which was to be used to study the carbon deposition and process variables (such as temperature distribution, temperature profile, the effect of poisoning, and life test). The second reactor is a continuous-stirred-tank-reactor (CSTR). In the CSTR the contents are thoroughly stirred so that the composition and temperature of the fluid are uniform throughout. Thus the exit stream has the same composition and temperature as the fluid inside the reactor.

The advantages of the CSTR are:

- Kinetics may be studied without any complicating control of the reaction rate by gas-solid mass or heat transfer which are encountered in a PBR.

• Bulk fluid temperature and concentration gradients are eliminated by the "perfect mixing" conditions.

• The temperature and concentration gradient between the bulk fluid and the catalyst surface are minimized.

• All but the fastest and most exothermic reactions can be studied at nearly isothermal conditions and nearly complete conversion.

• Perhaps most important the complicated reaction rate expression is induced to a much more accurate material-balance equation,

$$R = \frac{Q_i C_i - Q_o C_o}{W}$$

where, R = reaction rate, lb mol/hr-g of catalyst
Q = flow rate, SCF/hr
C = concentration, lb-mol/SCF
W = catalyst weight, g
i = inlet or feed
o = outlet or product

The CSTR is used to evaluate catalysts because it is the best available means to compare catalysts impartially on the same basis. The CSTR is used to study the temperature effects, the pressure effects, the kinetics of the reaction, and how components other than carbon monoxide affect the rate of methanation.

A schematic diagram of the CSTR is presented in Figure 5-1. Feed gas which can be premixed or not mixed is supplied from cylinders or trailers. The gas is metered by an orifice, rotometer and through the bypass, by the wet test meter. Product gas is cooled by a water condenser and measured by the wet test meter. The composition of the gas streams is analyzed by infrared analyzers for carbon monoxide and carbon dioxide. Composition is analyzed by a gas partitioner for carbon dioxide, nitrogen, carbon monoxide, methane, ethane and hydrogen if argon is used as the carrier gas for the instrument. Product gas is also collected in sampling bottles for mass spectrometer analysis of all components. Pressures are measured by gages throughout the system. Temperatures are measured by thermocouple-recorder and by potentiometer. The liquid sample is collected in the knockout pot and may be analyzed by wet chemistry.

The PBR is shown in Figure 5-2. It has the same arrangement as the CSTR except that there is a provision for steam injection. A sectioned view of the CSTR is presented in Figure 5-3 and the inserts for the reactor are shown in Figure 5-4. Two methods of catalyst mounting are employed. A catalyst can be placed in an annular basket or in a paddle-basket; the mounting systems are shown in Figure 5-5. When the paddle basket is utilized it replaces the radial impeller which is used only with the annular basket. The cylindrical wall and the top and bottom of the reactor each

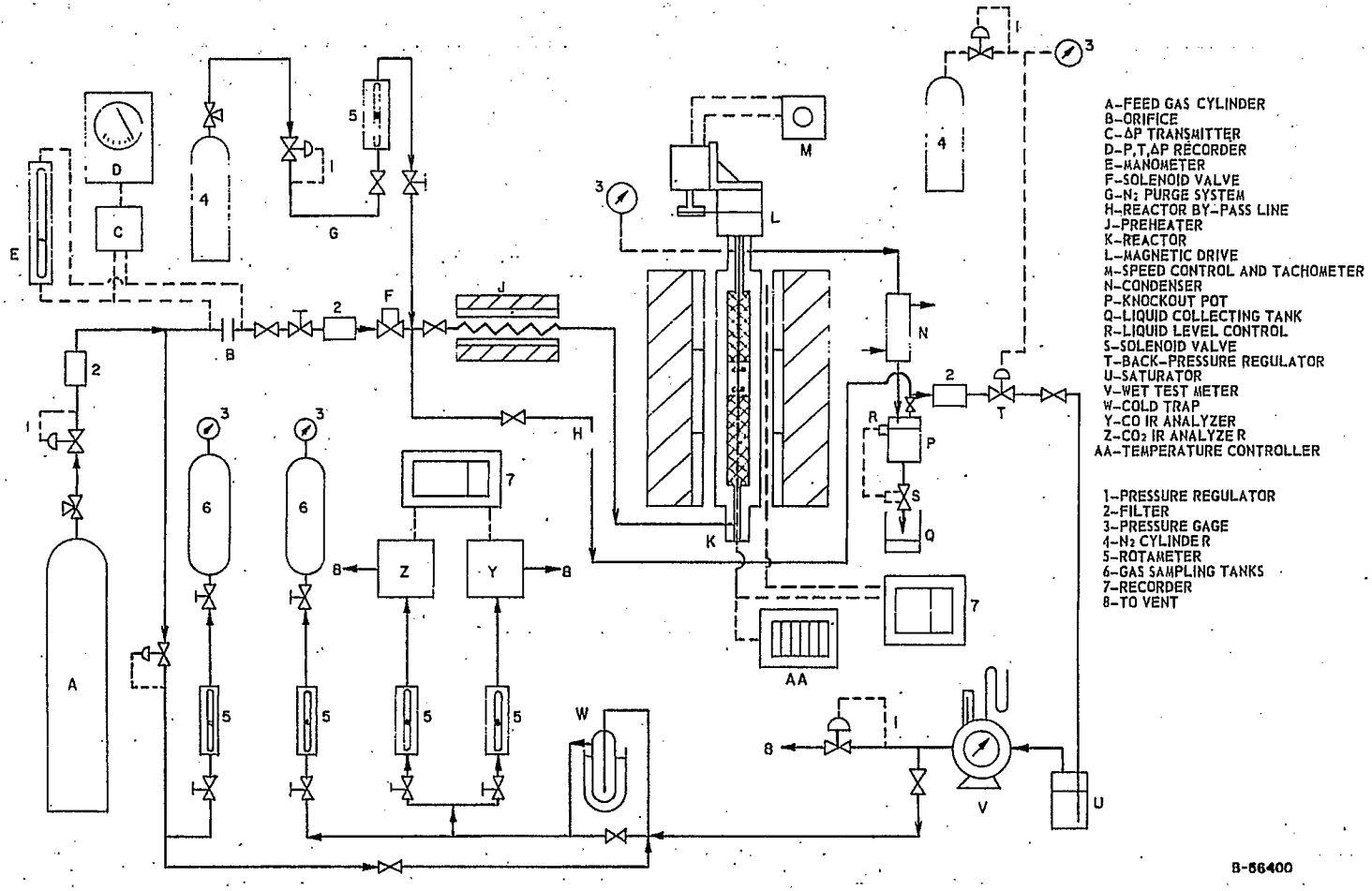

Figure 5-1. CONTINUOUS-STIRRED-TANK-REACTOR (CSTR) FOR HETEROGENEOUS CATALYSIS LABORATORY

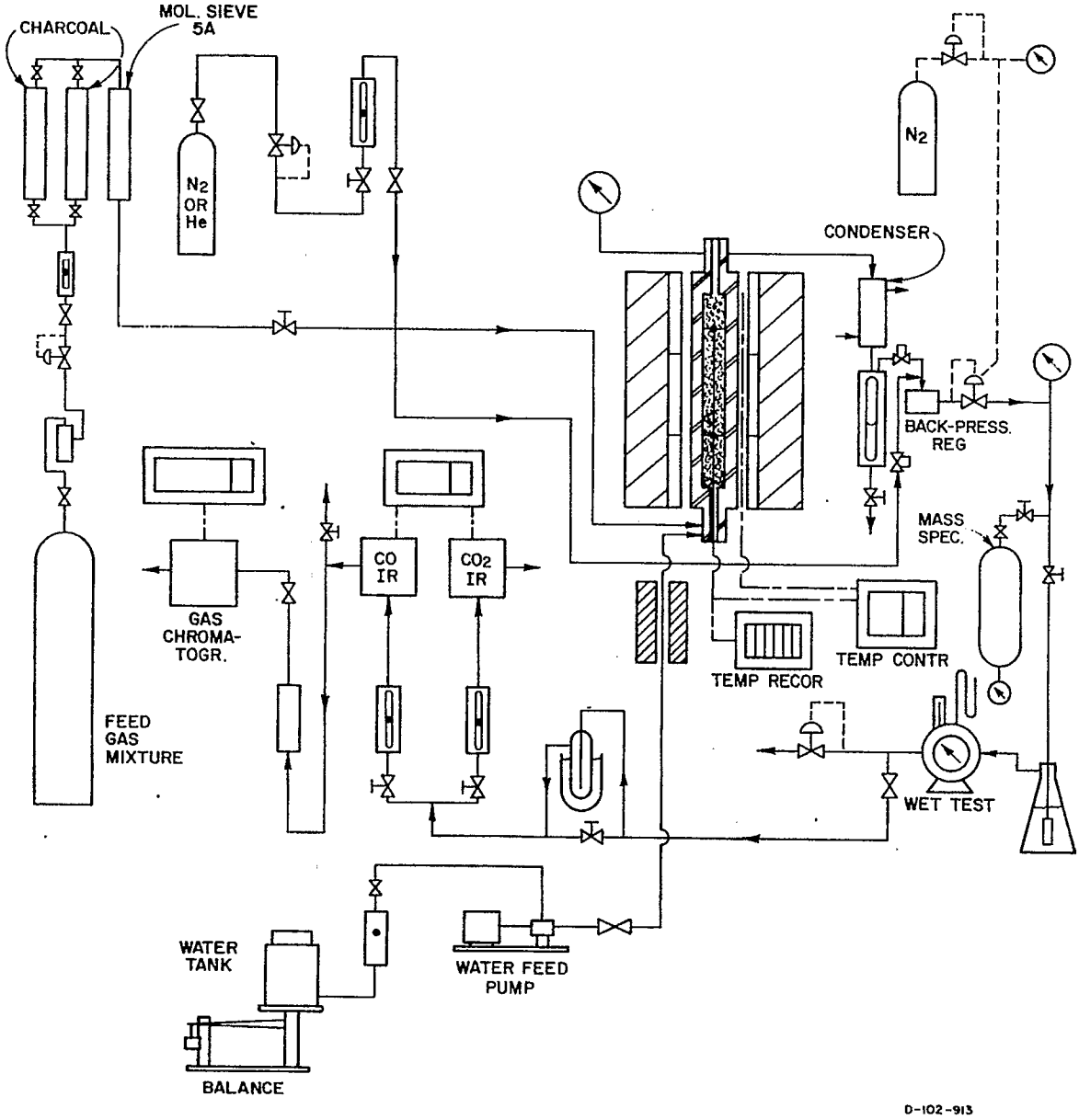

Figure 5-2. PACKED-BED REACTOR (PBR) FOR HETEROGENEOUS CATALYSIS LABORATORY

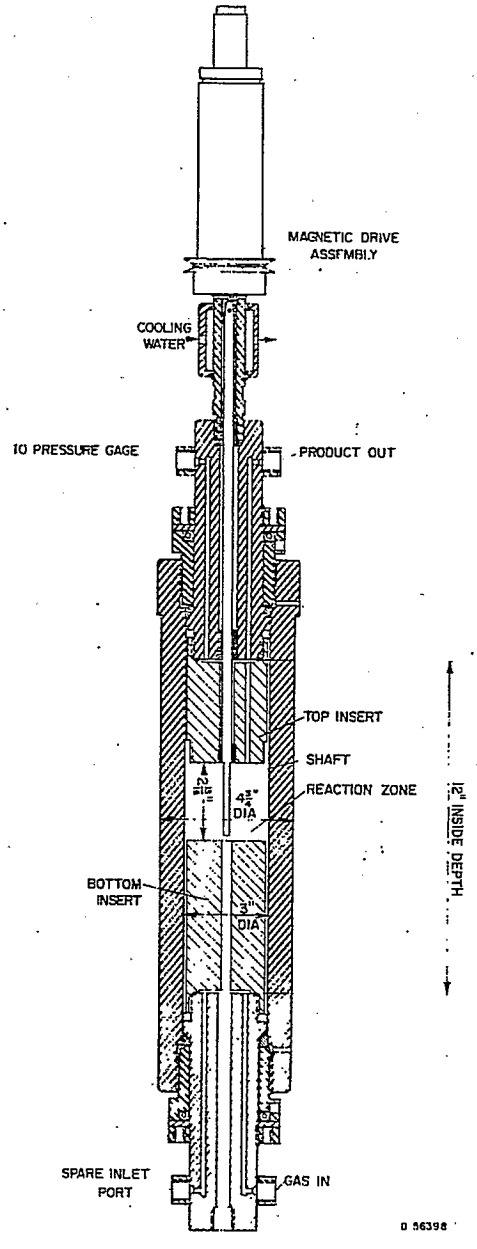

Figure 5-3. SECTIONAL VIEW OF CONTINUOUS-STIRRED-TANK-REACTOR

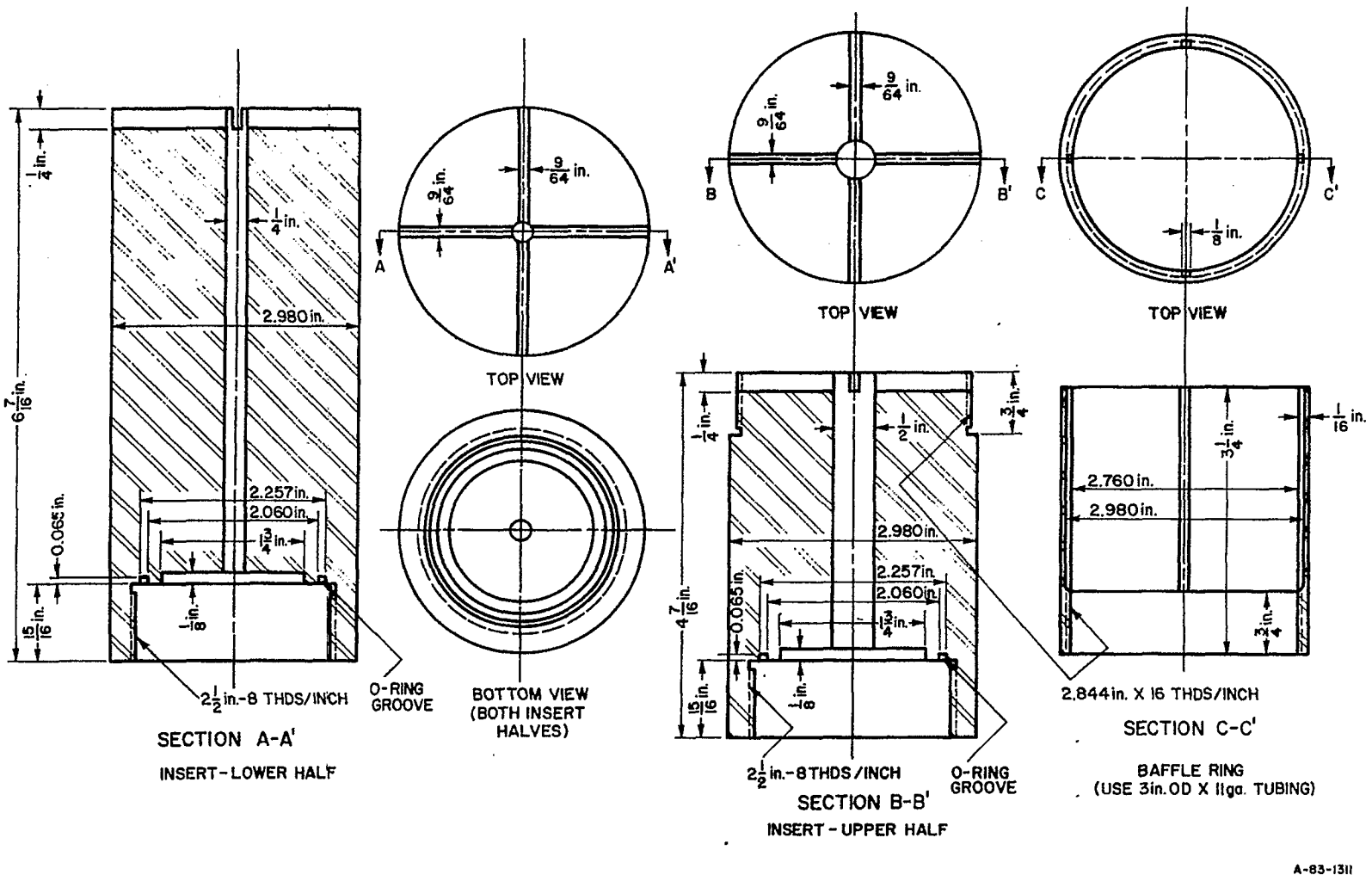

Figure 5-4. INSERTS FOR CONTINUOUS-STIRRED-TANK-REACTOR

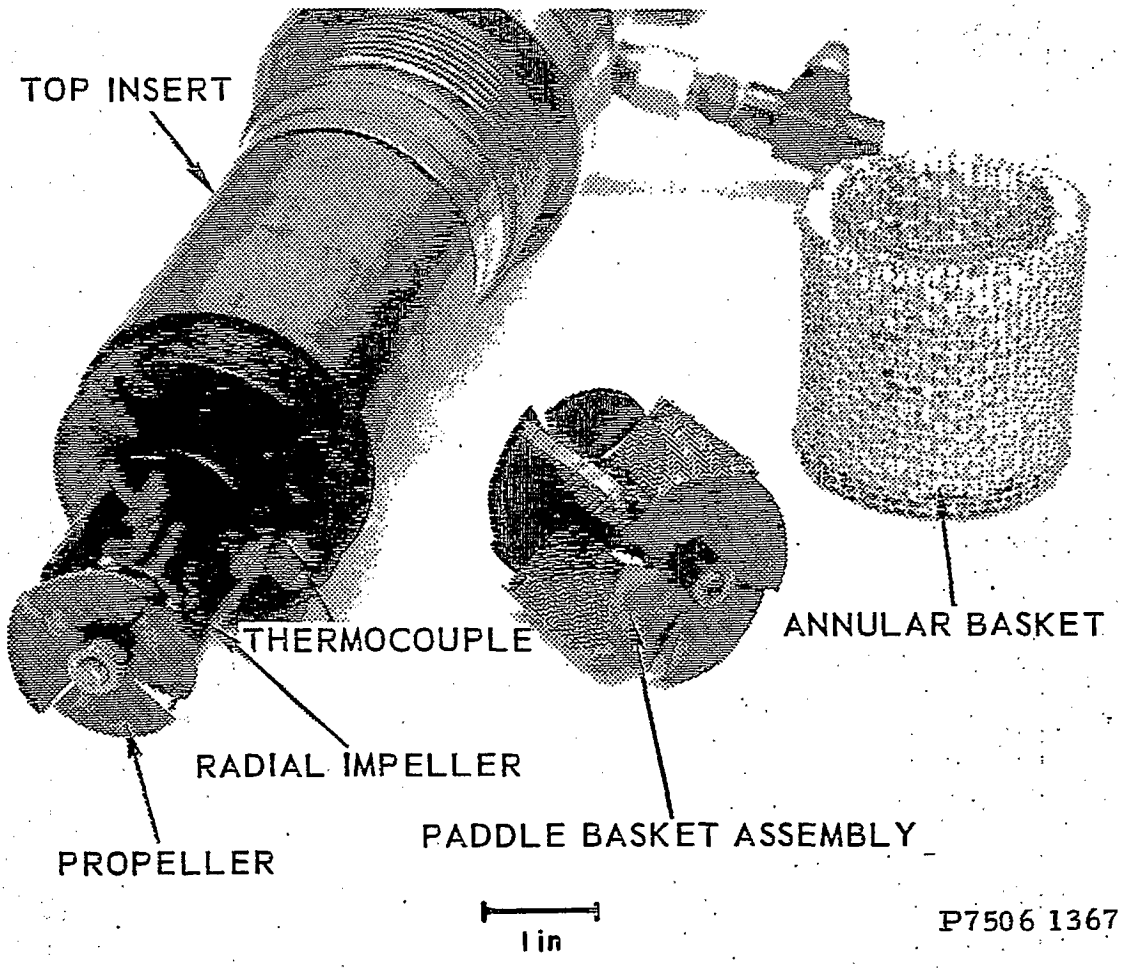

Figure 5-5. CATALYST MOUNTING METHODS

have four 0.125-inch wide baffles. The wall baffles extend along the total height of the stirred chamber; the top and bottom baffles extend radially to the cylindrical wall.

Catalyst temperatures are measured in the annular basket. Because the catalyst is stationary, a thermocouple is inserted in a hole drilled into the center of a catalyst.

A separate apparatus was set up for sulfur studies. The reactor and vessels were coated with Nucerite, a material that is inert to sulfur compounds. A schematic diagram of the sulfur study laboratory is presented in Figure 5-6.

5.2.1 Instrumentation

The pressures are measured by precision pressure gages which are accurate to 0.1%, the furnace temperatures are monitored by temperature-recorder and the reactor temperatures are measured by a K-3 potentiometer. The product gas flow is measured by wet test meter and the composition is measured by infrared analyzers, gas partitioner, and mass spectrometer. The carbon monoxide and carbon dioxide are monitored by the infrared analyzers continuously, all the components except hydrogen are measured by the gas partitioner when helium is used as the carrier gas and samples were taken from time to time for mass spectrometer analysis.

The measurement techniques described provided a triple check on the carbon oxides, and a double-check on all other components except hydrogen.

In order to measure concentrations less than 0.2 percent, it was necessary to re-span and adjust the infrared analyzers. Product water measurement is poor because of the condensation in the transferring lines and dead volume in the system that holds water.

5.3 Nonideal Flow Mixing Theory

The first thing to do after the reactor was built was to establish that the reactor is indeed a continuous-stirred-tank-reactor with complete mixing so that we may use the back-mixing model to evaluate catalysts and to study the kinetics. In order to prove that the CSTR possesses "perfect mixing" and to establish the "perfect mixing" zone, the stimulus-response technique was used. With regard to nonideal flow, this technique studies the age distribution function of a fluid either in a vessel or leaving a vessel. In preparation for the HYGAS research reported here, age-distribution studies were achieved by injecting a tracer into the reactor. Two methods were used to study the age distribution function of the tracer in the reactor. The methods are:

1) Pulse Test – A small amount of tracer was injected into the reactor over a short time; the response in the reactor effluent concentration of the tracer was then measured. For example, assume that nitrogen is flowing through the reactor at a given flow rate, pressure, temperature, and shaft speed. A known amount of carbon dioxide (the tracer) is injected into the reactor. The concentration of carbon dioxide leaving the reactor is continuously recorded such as shown in Figure 5-7. This is the age distribution function of the tracer in the reactor.

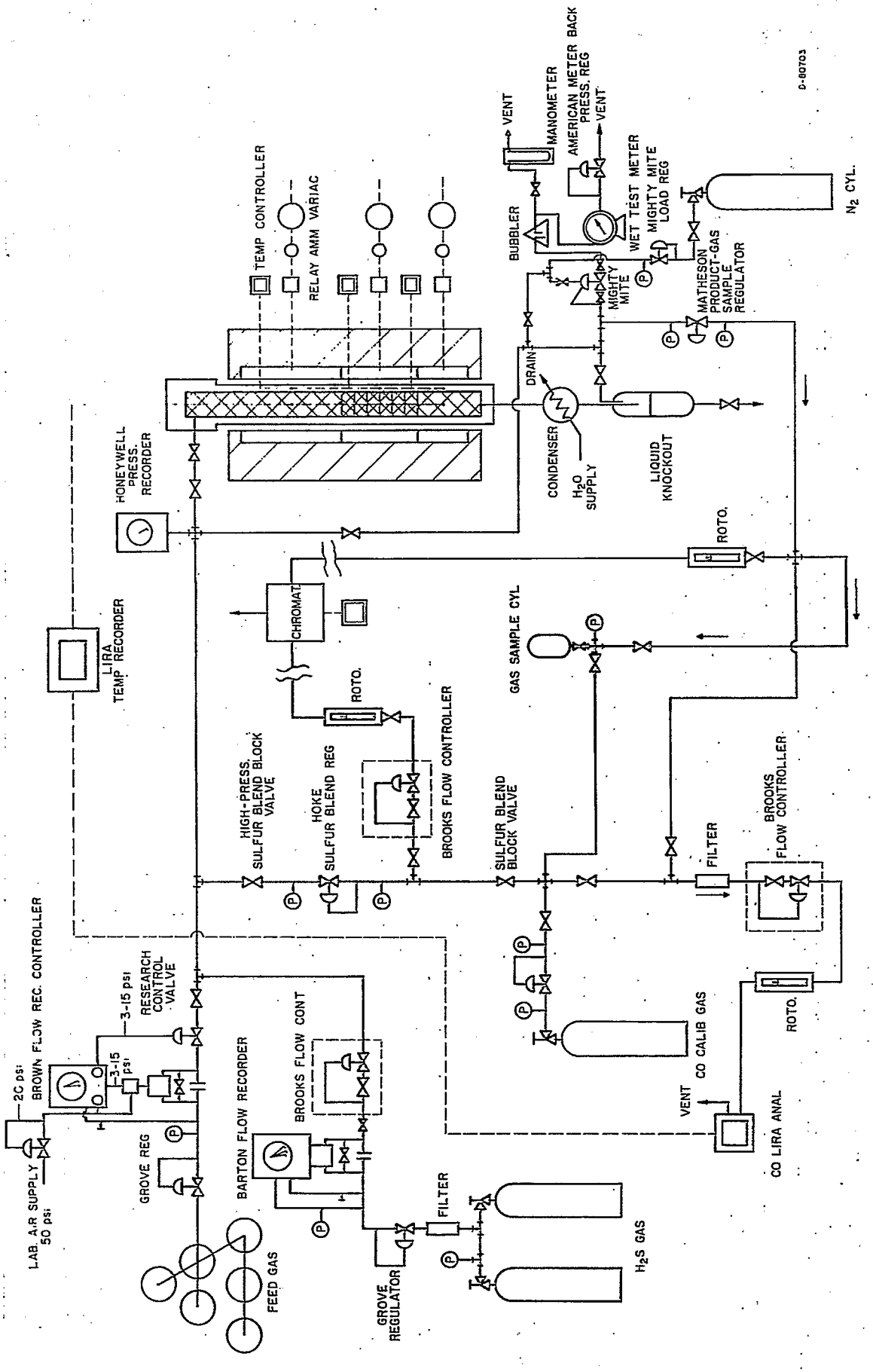

Figure 5-6. METHANATION CATALYST SULFUR TOLERANCE TESTING APPARATUS

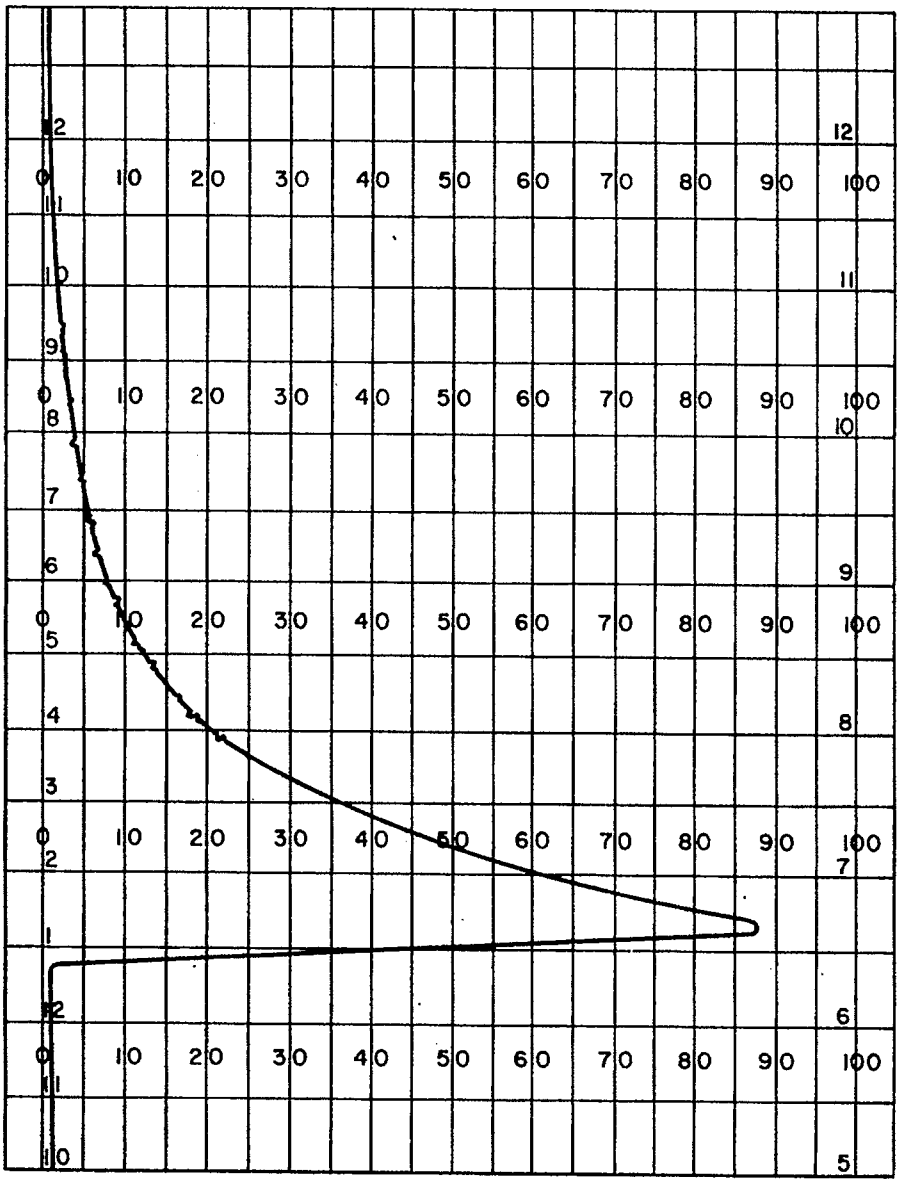

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Figure 5-7. ARTIST'S DRAWING OF TYPICAL RECORDED PULSE TEST RESPONSE

2) Step Test – The system is switched instantaneously from a steady flow of one gas to a steady flow of the tracer gas. For example, nitrogen flows just as it did in pulse test. Through a selector valve, carbon dioxide flowing into the reactor replaces nitrogen instantaneously. The carbon dioxide concentration in the product gas stream is continuously recorded. This is the age distribution function of the tracer in the reactor. After the tracer concentration reaches a maximum value, the response for any of these tests is an exponential decay of the tracer concentration with time. For the pulse test, the response is,

$$C/C_o = \exp(-tF/V)$$

Where, C = concentration of the tracer at any time t.
C_o = the maximum tracer concentration in the effluent.
t = time
F = flow rate
V = reactor volume.

For the step test, the response is,

$$1 - C/C_o = \exp(-tF/V)$$

Theoretically, it is "perfect mixing" if the slope is −1 and the area under the curve is 1 when ln C/Co is plotted versus tF/V.

Realistically, the area under the curve is seldom 1, because of dead volumes in the system and pre- or after-mixing in the lines causing delay of the tracer in the reactor system. If "perfect mixing" is achieved, however, the slope must be a straight line, as shown in Figure 5-8. The data for both 955 and 2250 rpm result in straight lines and indicate "perfect mixing"; data for 200 rpm result in a curved line – "imperfect" mixing.

In the HYGAS work discussed here, carbon monoxide and carbon dioxide were used as tracers, and nitrogen was used as inert gas. Flow rates of 0 to 40 standard cubic feet per hour, pressures from 0 to 1000 psig, and shaft speeds from 0 to 2500 rpm were the ranges investigated. Temperature did not affect the results because no chemical reaction occurred. "Perfect mixing" was achieved when shaft speed reached 1500 rpm for any pressure and flow rate. The "Perfect Mixing" zone is presented in Table 5-2. All test results are presented in Tables 5-3 and 5-4 and in Figures 5-9 to 5-13.

Imperfect mixing occurred at shaft speeds exceeding 2250 rpm. Shaft speeds recommended for experimental runs are listed in Table 5-2.

5.4 Equilibrium Compositions of Final Product in Methanation

Before beginning the experimental program on the catalyst evaluation and studies of kinetics, the possible gasification effluents or the possible feed compositions to the methanator should be analyzed for their equilibrium

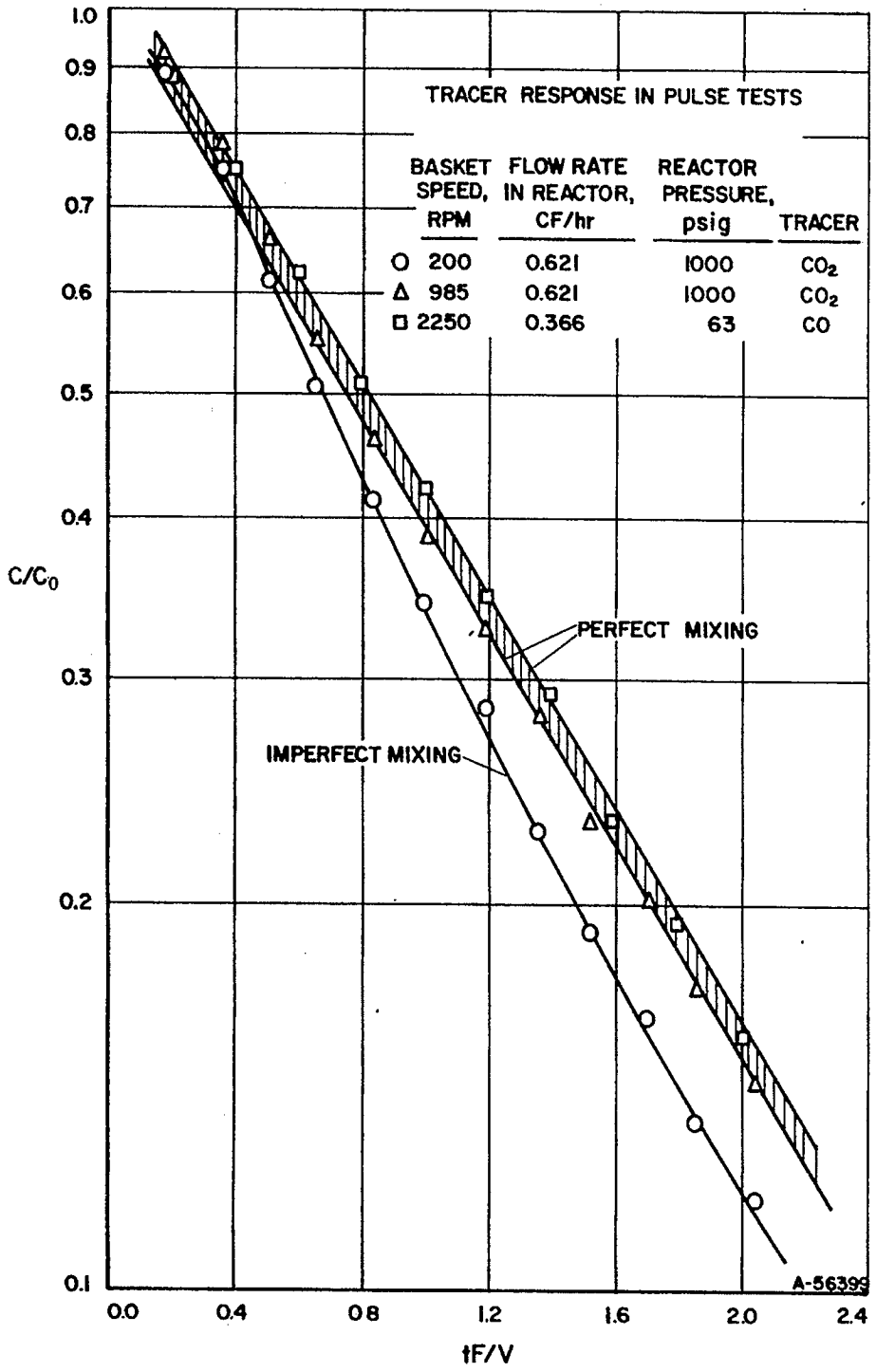

Figure 5-8. TYPICAL PULSE TEST RESULTS

conversions so that the final results can be estimated. The reactions that are most likely to take place in the methanator are:

$$CO + 3H_2 \overset{K_1}{\rightleftarrows} CH_4 + H_2O \quad (1)$$

$$CO + H_2O \overset{K_2}{\rightleftarrows} CO_2 + H_2 \quad (2)$$

$$CO_2 + 4H_2 \overset{K_3}{\rightleftarrows} CH_4 + 2H_2O \quad (3)$$

$$C_2H_6 + H_2 \overset{K_4}{\rightleftarrows} 2CH_4 \quad (4)$$

$$C_3H_6 + 2H_2 \overset{K_5}{\rightleftarrows} 3CH_4 \quad (5)$$

$$CO + H_2 \overset{K_6}{\rightleftarrows} C + H_2O \quad (6)$$

$$2CO \overset{K_7}{\rightleftarrows} C + CO_2 \quad (7)$$

$$CH_4 \overset{K_8}{\rightleftarrows} C + 2H_2 \quad (8)$$

Table 5-2. "PERFECT MIXING" RANGE FOR HYGAS-ASSOCIATED CONTINUOUS-STIRRED-TANK-REACTOR

Pressure atm	Pressure psig	Flow Rate Minimum SCF/Hr	Flow Rate Maximum SCF/Hr	Shaft Speed Minimum rpm
1	0.0	0.0725	0.58	500
2	14.7	0.1450	1.16	1000
5	58.8	0.362	2.90	1000
10	132.3	0.725	5.80	1000
20	279.3	1.450	11.60	1000
30	426.3	2.175	17.4	1500
40	573.3	2.900	23.2	1500
50	720.3	3.620	29.0	1500
60	867.3	4.35	34.8	1500
69	999.6	5.00	40.0	1500

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Table 5-3. PULSE TEST TO ESTABLISH THE "PERFECT MIXING" ZONE

Run No.	1		2		3			4		5		6			7		8		9		10	
Press., psig	63		63		63			63		63		63			65		65		65		65	
Shaft Speed, rpm	2250		1750		1250			2250		1450		750			2250		2250		1450		750	
tf/v	C, mol%	C/Co	C, mol%	C/Co	C, mol%	C/Co	tf/v	C, mol%	C/Co	C, mol%	C/Co	C, mol%	C/Co	tf/v	C, mol%	C/Co	C, mol%	C/Co	C, mol%	C/Co	C, mol%	C/Co
0	3.16	1.000	2.34	1.000	3.18	1.000	0	2.90	1.000	2.90	1.000	2.96	1.000	0	2.86	1.000	2.82	1.000	2.86	1.000	2.92	1.000
0.199	2.80	0.886	2.06	0.880	2.72	0.855	0.234	2.56	0.882	2.56	0.882	2.56	0.865	0.316	2.37	0.829	2.34	0.830	2.37	0.829	2.39	0.819
0.398	2.37	0.750	1.73	0.740	2.26	0.710	0.468	2.15	0.742	2.13	0.735	2.13	0.720	0.632	1.87	0.654	1.82	0.645	1.84	0.645	1.87	0.640
0.597	1.97	0.623	1.43	0.610	1.87	0.588	0.702	1.78	0.614	1.75	0.603	1.75	0.592	0.948	1.45	0.507	1.41	0.500	1.41	0.493	1.43	0.490
0.796	1.61	0.510	1.17	0.500	1.52	0.478	0.936	1.43	0.493	1.44	0.497	1.43	0.484	1.26	1.13	0.396	1.08	0.383	1.08	0.378	1.08	0.370
0.995	1.34	0.424	0.96	0.410	1.27	0.400	1.17	1.17	0.404	1.18	0.407	1.17	0.396	1.58	0.87	0.304	0.84	0.298	0.83	0.290	0.83	0.284
1.194	1.10	0.348	0.77	0.329	1.02	0.321	1.40	0.96	0.331	0.97	0.335	0.96	0.324	1.90	0.66	0.231	0.64	0.227	0.62	0.217	0.62	0.212
1.393	0.92	0.291	0.64	0.274	0.85	0.267	1.64	0.77	0.266	0.79	0.273	0.77	0.260	2.21	0.51	0.178	0.48	0.170	0.47	0.164	0.48	0.165
1.592	0.74	0.234	0.52	0.222	0.68	0.214	1.87	0.62	0.214	0.64	0.221	0.62	0.210	2.53	0.38	0.133	0.36	0.128	0.36	0.126	0.36	0.123
1.792	0.61	0.193	0.42	0.180	0.56	0.176	2.11	0.50	0.172	0.52	0.179	0.51	0.172	2.84	0.30	0.105	0.28	--	--	--		
1.990	0.50	0.158	0.34	0.145	0.46	0.145	2.34	0.40	0.138	0.42	0.145	0.40	0.135									
2.189	0.41	0.130			0.37	0.116	2.57	0.35	0.121	0.36	0.124	0.34	0.115									

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Table 5-4. STEP TEST TO ESTABLISH THE "PERFECT MIXING" ZONE

Run No.	11		12		13		14		15		16	
Pressure, psig	1000		1000		1000		1000		1000		1000	
Shaft Speed, rpm	2520		2530		2530		1440		0		1440	
tf/v	C, mol%	C/Co	C, mol%	1-C/Co	C, mol%	C/Co	C, mol%	1-C/Co	C, mol%	C/Co	C, mol%	C/Co
0	9.85	1.000	0.000	1.000	9.85	1.000	0.000	1.000	9.85	1.000	9.85	1.000
0.188	8.46	0.860	1.18	0.880	8.80	0.894	2.35	0.761	8.15	0.827	8.00	0.812
0.376	7.30	0.741	2.38	0.758	7.80	0.791	4.34	0.559	6.78	0.688	6.60	0.670
0.564	6.29	0.638	3.39	0.656	6.85	0.695	5.75	0.416	5.70	0.579	5.38	0.546
0.752	5.46	0.554	4.20	0.573	6.15	0.625	6.68	0.321	4.82	0.490	4.58	0.465
0.940	4.75	0.482	4.87	0.506	5.50	0.559	7.53	0.235	4.04	0.410	3.80	0.386
1.128	4.13	0.419	5.45	0.447	4.98	0.505	8.10	0.178	3.39	0.344	3.06	0.310
1.316	3.56	0.361	5.98	0.394	4.44	0.450	8.55	0.131	8.70	0.274	2.46	0.250
1.504	3.07	0.312	6.40	0.350	3.95	0.401	8.85	0.100	2.35	0.239	2.00	0.203
1.692	2.65	0.269	6.80	0.310	3.52	0.358	9.12	0.073	1.97	0.200	1.60	0.162
1.880	2.28	0.232	7.15	0.274	3.16	0.321			1.60	0.162	1.26	0.128
2.068	1.96	0.199	7.45	0.244	2.85	0.289			1.35	0.137	0.98	0.099
2.256	1.69	0.172	7.73	0.215	2.50	0.254			1.08	0.110		
2.444	1.45	0.147	7.98	0.190	2.25	0.228						
2.632	1.24	0.126	8.20	0.168	1.97	0.200						
2.820	1.08	0.110	8.40	0.147	1.76	0.179						
3.008	0.93	0.094	8.57	0.130	1.54	0.156						

Table 5-4, Part 2. STEP TEST TO ESTABLISH THE "PERFECT MIXING" ZONE

Run No.	23		24			25			26		
Pressure, psig	995		995			995			995		
Shaft Speed, rpm	2500		2000			2000			1000		
tf/v	C, mol%	1 - C/Co	tf/v	C, mol%	C/Co	tf/v	C, mol%	1 - C/Co	tf/v	C, mol%	C/Co
0.000	0.00	1.000	0.00	5.10	1.000	0.000	0.00	1.000	0.000	5.10	1.000
0.194	0.78	0.847	0.23	4.36	0.855	0.299	0.64	0.874	0.157	4.52	0.886
0.388	1.46	0.714	0.46	3.591	0.704	0.598	1.24	0.757	0.314	3.98	0.780
0.582	2.01	0.606	0.69	2.93	0.575	0.898	1.80	0.647	0.471	3.44	0.675
0.776	2.47	0.516	0.92	2.42	0.475	1.197	2.18	0.572	0.628	2.99	0.586
0.970	2.86	0.439	1.15	2.00	0.392	1.496	2.60	0.490	0.785	2.60	0.510
1.165	3.22	0.369	1.38	1.68	0.329	1.795	2.96	0.420	0.942	2.27	0.445
1.359	3.50	0.314	1.61	1.41	0.276	2.09	3.26	0.360	1.099	1.99	0.390
1.553	3.75	0.265	1.84	1.20	0.236	2.39	3.48	0.317	1.26	1.75	0.343
1.747	3.95	0.225	2.07	1.00	0.196	2.69	3.71	0.273	1.41	1.54	0.302
1.941	4.13	0.190	2.30	0.85	0.167	2.99	3.90	0.235	1.57	1.36	0.267
2.135	4.28	0.161	2.53	0.72	0.141	3.29	4.05	0.205	1.73	1.21	0.238
2.329	4.40	0.137	2.76	0.61	0.120	3.59	4.19	0.179	1.88	1.06	0.208
2.523	4.48	0.122	2.99	0.51	0.100	3.89	4.31	0.155	2.04	0.95	0.186
2.717	4.60	0.098	3.22	0.42	0.082	4.19	4.40	0.137	2.20	0.85	0.167
2.912	4.68	0.082				4.49	4.50	0.118	2.36	0.76	0.149
3.106	4.74	0.071				4.79	4.56	0.105	2.51	0.68	0.133
3.300	4.80	0.059				5.09	4.63	0.091	2.67	0.60	0.118
3.494	4.85	0.049				5.39	4.69	0.080	2.83	0.54	0.106
3.688	4.89	0.041				5.68	4.74	0.070	2.98	0.49	0.096
						5.98	4.80	0.059	3.14	0.44	0.086

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Table 5-4, Part 3. STEP TEST TO ESTABLISH THE "PERFECT MIXING" ZONE

Run No.	17			18			19			20			21			22		
Pressure, psig	1000			1000			1000			1000			1000			1000		
Shaft Speed, rpm	2300			2300			2300			2300			2300			2300		
tf/v	C, mol%	1-C/Co	tf/v	C, mol%	C/Co	tf/v	C, mol%	C/Co	tf/v	C, mol%	1-C/Co	tf/v	C, mol%	C/Co	tf/v	C, mol%	C/Co
0.000	0.00	1.000	0.000	5.10	1.000	0.000	5.10	1.000	0.00	0.00	1.000	0.000	5.10	1.000	0.000	5.10	1.000
0.125	0.57	0.888	0.183	4.39	0.861	0.23	4.15	0.814	0.35	1.21	0.763	0.334	3.82	0.749	0.122	4.55	0.892
0.250	1.04	0.796	0.366	3.80	0.745	0.46	3.39	0.665	0.70	2.18	0.572	0.668	2.83	0.555	0.244	4.17	0.817
0.375	1.22	0.761	0.549	3.24	0.635	0.69	2.77	0.543	1.05	2.95	0.421	1.002	2.10	0.412	0.366	3.82	0.750
0.500	1.80	0.647	0.732	2.75	0.539	0.92	2.26	0.444	1.40	3.51	0.311	1.336	1.59	0.312	0.488	3.48	0.682
0.625	2.13	0.582	0.915	2.34	0.459	1.15	1.85	0.363	1.75	3.88	0.239	1.670	1.21	0.237	0.610	3.18	0.624
0.750	2.41	0.527	1.098	2.01	0.394	1.38	1.54	0.302	2.10	4.19	0.178	2.004	0.93	0.182	0.732	2.90	0.569
0.875	2.69	0.472	1.281	1.73	0.339	1.61	1.28	0.251	2.45	4.40	0.137	2.338	0.70	0.137	0.854	2.64	0.518
1.000	2.95	0.422	1.464	1.55	0.304	1.84	1.07	0.210	2.80	4.55	0.108	2.672	0.55	0.108	0.976	2.40	0.471
1.125	3.17	0.379	1.647	1.30	0.255	2.07	0.89	0.175	3.15	4.67	0.085				1.098	2.19	0.430
1.250	3.37	0.340	1.830	1.14	0.224	2.30	0.74	0.145	3.50	4.76	0.066				1.220	1.96	0.384
1.375	3.54	0.306	2.013	0.98	0.192	2.53	0.62	0.122	3.85	5.10	0.000				1.342	1.77	0.347
1.500	3.70	0.275	2.196	0.85	0.167	2.76	0.51	0.100							1.464	1.60	0.314
1.625	3.83	0.249	8.379	0.74	0.145	2.99									1.586	1.44	0.282
1.750	3.96	0.224	2.562	0.64											1.708	1.30	0.255
1.875	4.07	0.202													1.830	1.19	0.234
2.000	4.16	0.184													1.957	1.07	0.210
2.125	4.24	0.169													2.074	0.98	0.192
2.250	4.32	0.153													2.196	0.88	0.173
2.375	4.39	0.139													2.318	0.80	0.157
2.500	4.46	0.125													2.440	0.72	0.141
2.625	4.52	0.114															
2.750	4.57	0.104															

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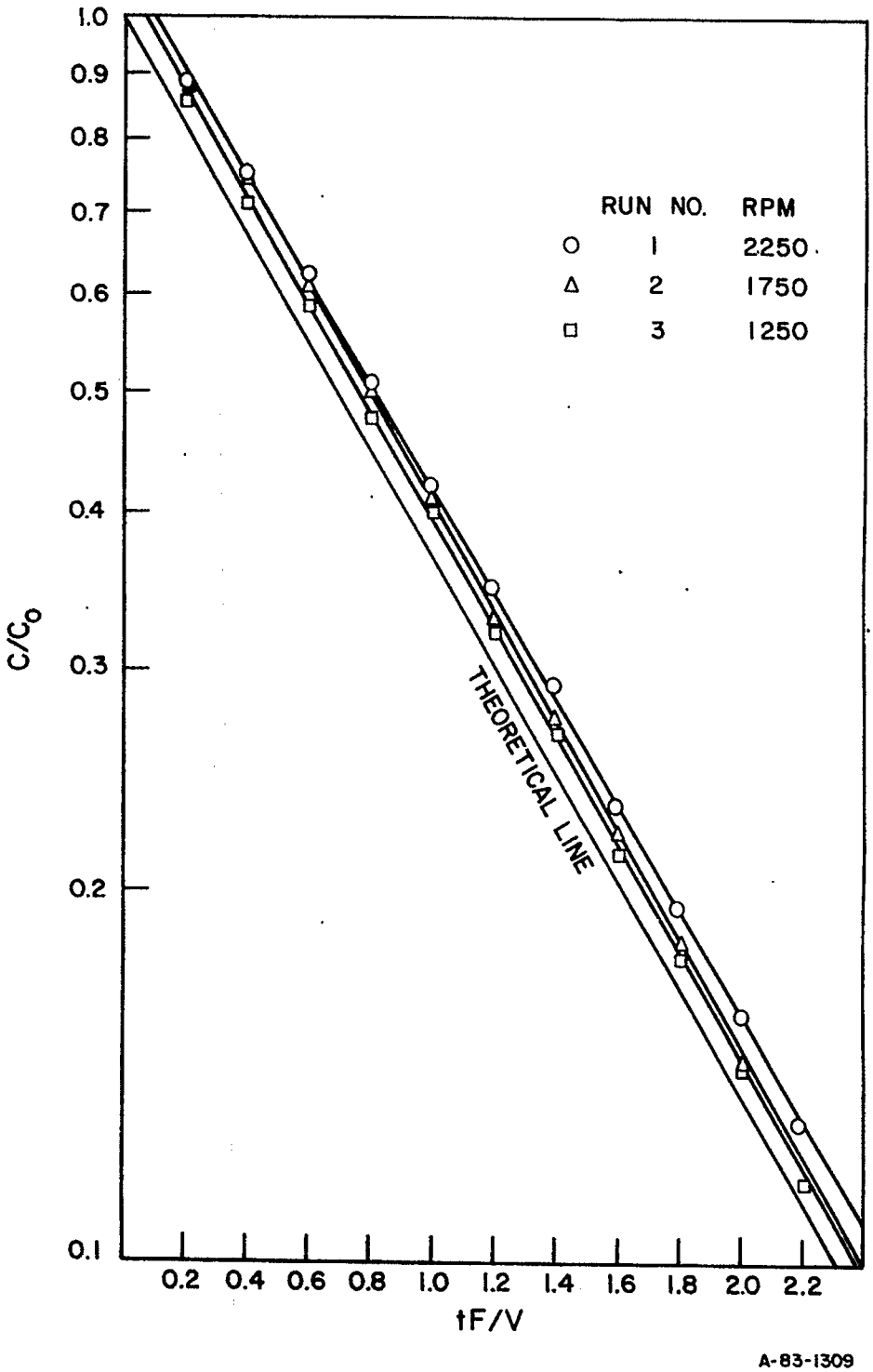

Figure 5-9. PULSE TEST AT 63 psig

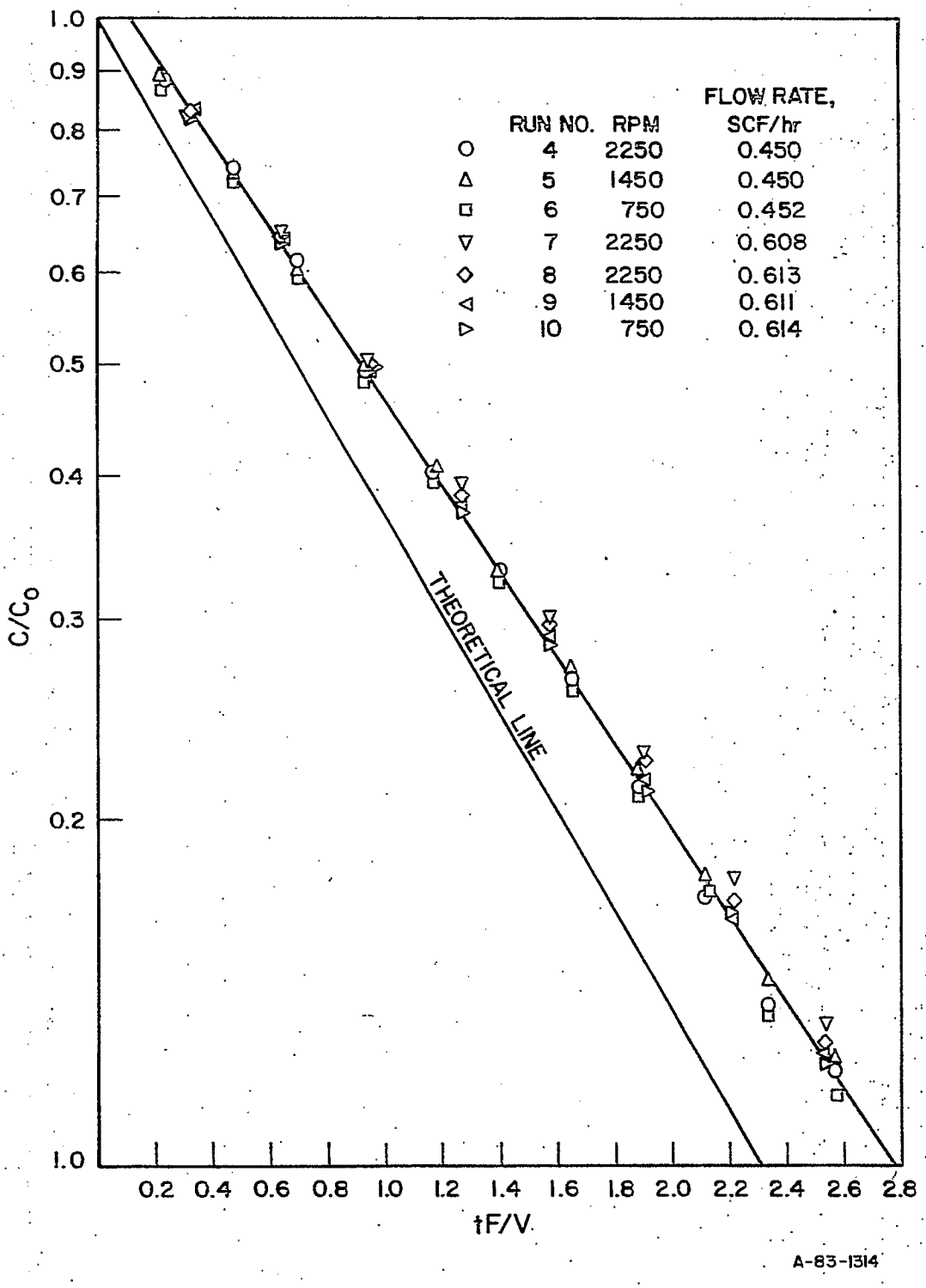

Figure 5-10. PULSE TEST AT 63 psig

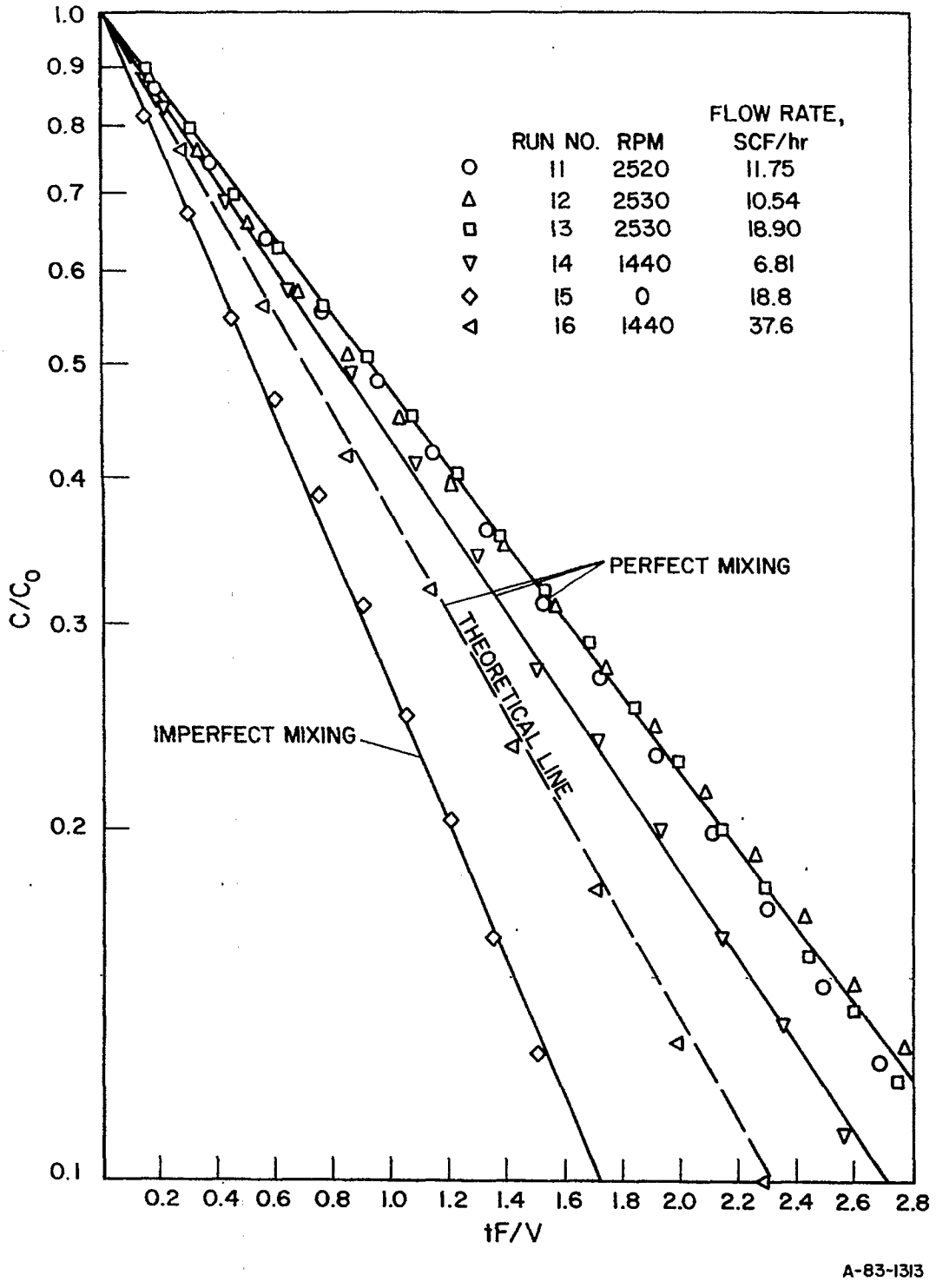

Figure 5-11. STEP TEST AT 1000 psig

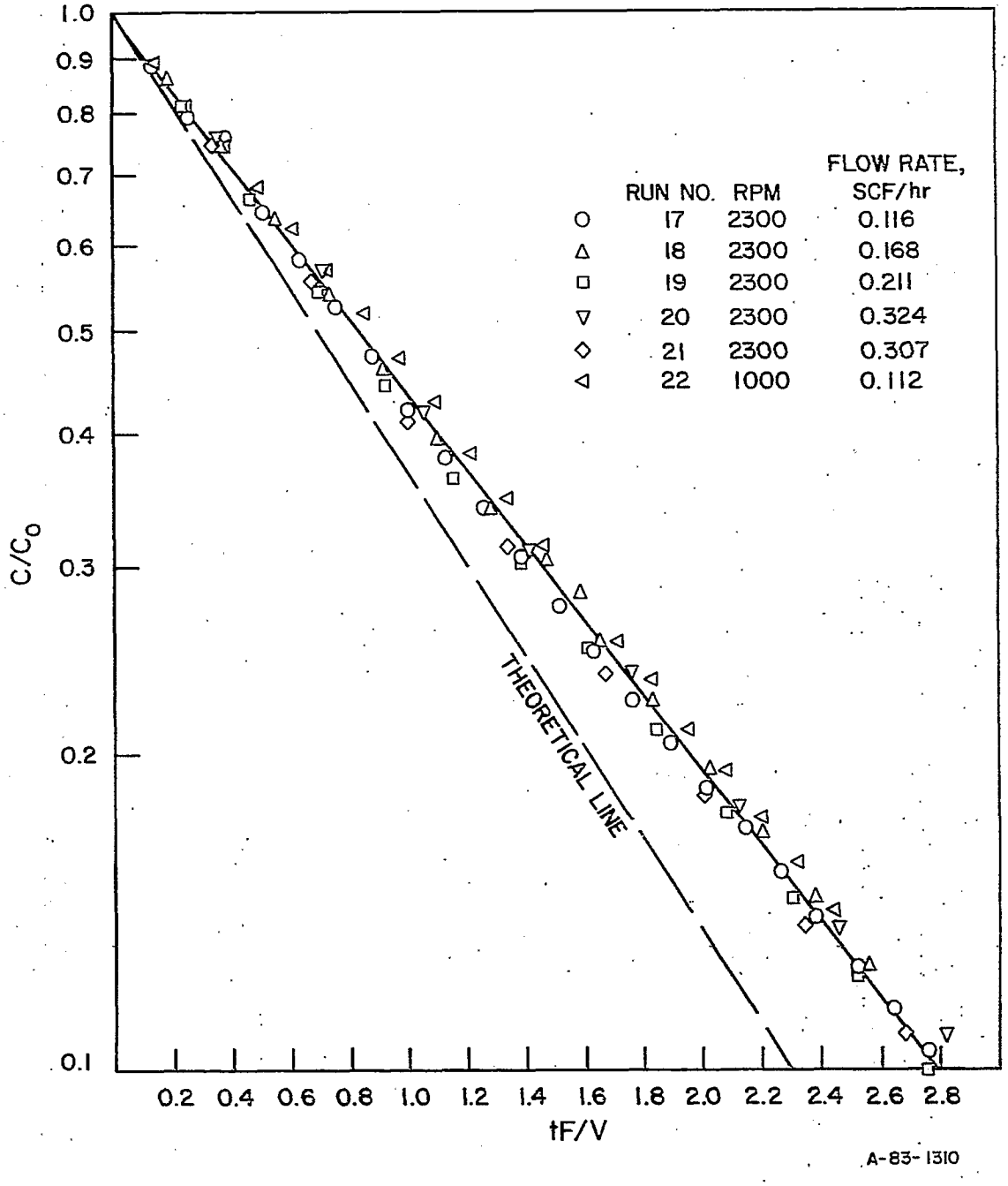

Figure 5-12. STEP TEST AT 1000 psig

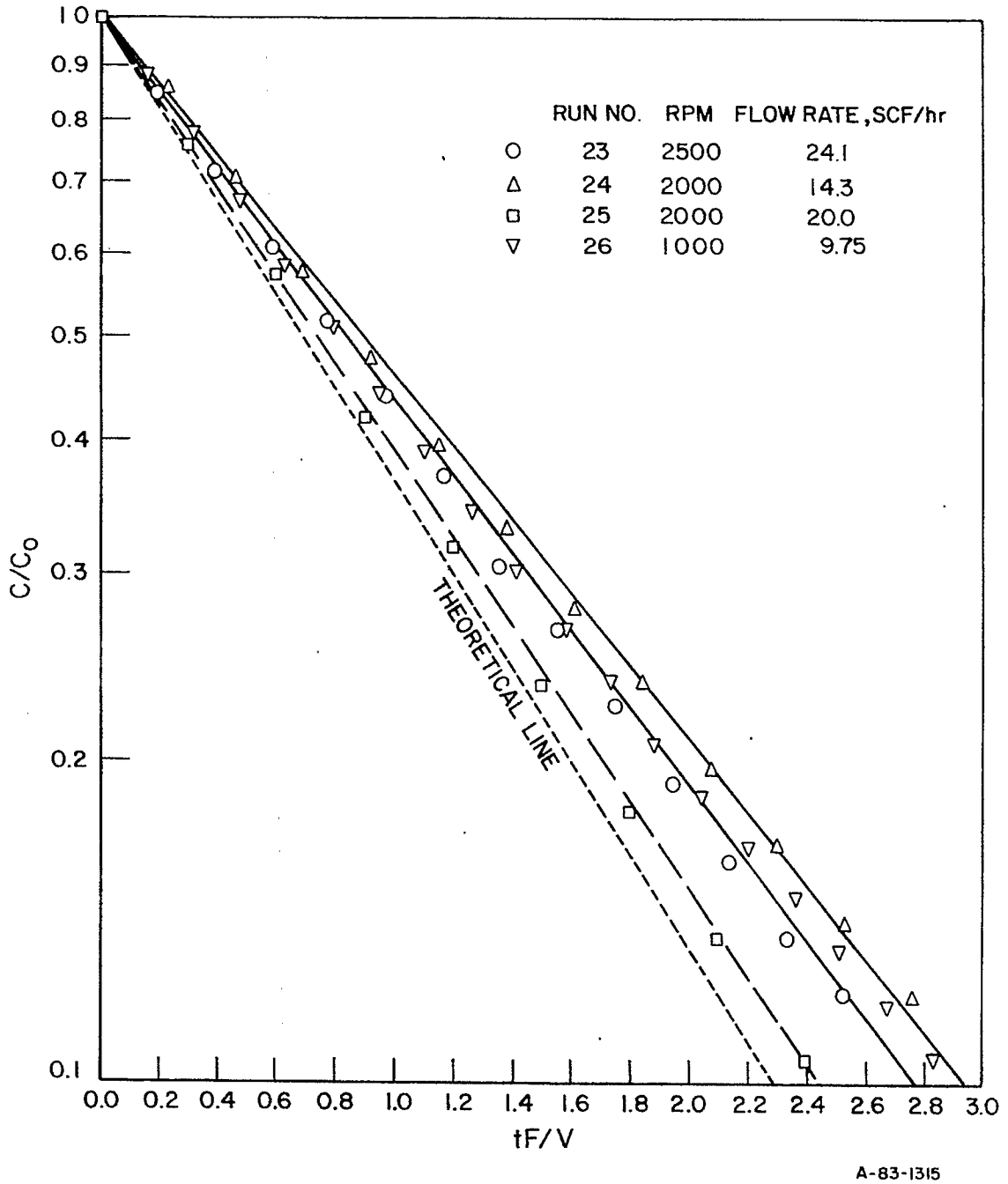

Figure 5-13. STEP TEST AT 995 psig

The free energy of reaction or the equilibrium constant is needed for each of the above reactions to estimate the product compositions in the methanator at equilibrium. Ideal gas equilibrium constants[1] were used in the work presented here. Attempts were made to correlate the real gas equilibrium constants with the Benedict-Webb-Rubin, Chao-Seader, and Redlich-Kwong equations of State. The lack of high-pressure data on hydrogen, carbon monoxide and carbon dioxide prevents an accurate prediction. For those who wish to investigate further, however, the program by Chemshare[2] may be a starting point.

Equations 1 to 5 are considered for the composition analysis. Equations 6 to 8 are the carbon deposition reactions and will be considered in the following section. The ideal gas equilibrium constants and heats of reaction were correlated by a linear regression method (Appendix 5-A). The developed coefficients are presented in Table 5-5 with the standard deviations also shown in this table. The equilibrium constants of these reactions are presented in Figure 5-14. The analysis of product components is presented in Table 5-6 in which are the unknowns. These unknowns are solved by a subprogram called solution of simultaneous equations of several unknowns (Appendix 5-B) and this program is presented in Table 5-7. Equilibrium compositions for typical HYGAS products at 1000 psig are presented in Table 5-8. Based on these results, it may be concluded that ethane and propane hydrogenolysis is highly favored at HYGAS conditions and for reduction of carbon monoxide to less than 0.1%, the reaction temperature must be less than 1000°F for a single reactor.

5.4.1 Carbon Deposition

Thermodynamics favors carbon deposition in the reactor at the methanation conditions as shown in Figure 5-14. Low temperature favors carbon deposition by reactions 6 and 7, and high temperature favors carbon deposition by reaction 8. The temperature in the reactor increases as more carbon monoxide is converted to methane. Consequently, methane decomposition is most likely to occur near the outlet of the reactor, and carbon monoxide decomposition is likely to occur near the inlet of the reactor, where the carbon monoxide content of the gas is high and the reactor temperature is relatively low.

5.4.2 Metal Carbonyl Formation

Most carbonyls are very toxic and formation of a metal carbonyl from a metal catalyst means loss of activity. The carbonyls of Ni, Fe, and Co are the most common. Those of Cr, Mo, W, Re, Ru, Rh, Os, Ir, and Mn are also readily found. Most methanation catalysts contain these metals and the catalyst formulation is ideally suited for producing carbonyls. Some of the physical properties of metal carbonyls are presented in Table 5-9.

5.5 Catalyst Evaluation

5.5.1 Method of Evaluation

Each catalyst was studied according to the sequence of procedures listed in section 5.1 Introduction. The study was discontinued at the step

Table 5-5, Part 1. IDEAL GAS EQUILIBRIUM CONSTANTS EQUATION FOR METHANATION REACTION, $CO + 3H_2 \rightleftarrows CH_4 + H_2O$

```
          TEMP          INLC5 SUBROUTINE FOR DATA INPUT FOR LRMC5   10/13/67

      SUBROUTINE INLC5(X,WT)
C     DEFINE X ARRAY AND WEIGHT  (WT)
C     SET X(NP+1) = DEPENDENT VARIABLE
C         **********
      DIMENSION X(31)
      IOUT = 5
      READ (2,10) Y,T
      WRITE (IOUT,900) Y,T
      T=T+459.67
      X(1)=1.
      X(2)=1./T
      X(3)=T
      X(4)=T*T
      X(5)=Y
      WT=1.0
      RETURN
   10 FORMAT (F15.4,F10.1)
  900 FORMAT (3H Y=F15.4,6X,2HT=F10.1)
      END
VARIABLE ALLOCATIONS
     Y(R )=0000          T(R )=0002       IOUT(I )=0004

STATEMENT ALLOCATIONS
 10   =001C  900  =0013

FEATURES SUPPORTED
 ONE WORD INTEGERS

CALLED SUBPROGRAMS
 FADD    FMPY    FDIV    FLD     FSTO    FSTOX   SRED    SWRT    SCOMP   SIOF    SUBIN

REAL CONSTANTS
  .459670E 03=000A    .100000E 01=000C

INTEGER CONSTANTS
     5=000E      2=000F

CORE REQUIREMENTS FOR INLC5
 COMMON      0  VARIABLES     10  PROGRAM     94

RELATIVE ENTRY POINT ADDRESS IS 001C (HEX)

END OF COMPILATION

// DUP

*STORE      WS  UA  INLC5
CART ID 0001   DB ADDR  4835   DB CNT   0008

// XEQ LRMC5
```

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Table 5-5, Part 2. IDEAL GAS EQUILIBRIUM CONSTANTS
EQUATION FOR METHANATION REACTION $CO + 3H_2 \rightleftarrows CH_4 + H_2O$

```
  4   8
PI= 0.05000      PO= 0.05000
Y=          8.6629       T=      500.0
Y=          6.6603       T=      600.0
Y=          4.9895       T=      700.0
Y=          3.5753       T=      800.0
Y=          2.3627       T=      900.0
Y=          1.3098       T=     1000.0
Y=          0.3874       T=     1100.0
Y=         -0.4279       T=     1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


 2    0.4884278E 04   0.1083E 04      0.2455E 01


 1   -0.1286844E 02   0.4436E-01
 2    0.2068898E 05   0.5538E 02      0.2240E-01


 1   -0.1161675E 02   0.2742E 00
 2    0.1991435E 05   0.1712E 03
 3   -0.4894912E-03   0.1069E-03      0.1079E-01


  I   A(I)            VARIANCE        STANDARD DEVIATION

  1  -0.1161E 02     0.7520E-01      0.2742E 00
  2   0.1991E 05     0.2934E 05      0.1712E 03
  3  -0.4894E-03     0.1143E-07      0.1069E-03
                     0.1164E-03      0.1079E-01

CORRELATION COEFF. ARRAY
 1 1.000-0.996-0.996
 2-0.996 1.000 0.987
 3-0.996 0.987 1.000

COVARIANCE ARRAY
 1 0.752E-01-0.468E 02-0.292E-04
 2-0.468E 02 0.293E 05 0.180E-01
 3-0.292E-04 0.180E-01 0.114E-07

  K   Y OBSERVED    Y COMPUTED     DIFF.          WEIGHTING FACTOR
  1   0.8662E 01    0.8664E 01   -0.1842E-02      0.1000E 01
  2   0.6660E 01    0.6657E 01    0.2779E-02      0.1000E 01
  3   0.4989E 01    0.4988E 01    0.1475E-02      0.1000E 01
  4   0.3575E 01    0.3575E 01   -0.5273E-03      0.1000E 01
  5   0.2362E 01    0.2364E 01   -0.1456E-02      0.1000E 01
  6   0.1309E 01    0.1311E 01   -0.1999E-02      0.1000E 01
  7   0.3874E 00    0.3881E 00   -0.7101E-03      0.1000E 01
  8  -0.4279E 00   -0.4301E 00    0.2266E-02      0.1000E 01

VAR. Y= 0.5068E-05
```

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Table 5-5, Part 3. IDEAL GAS EQUILIBRIUM CONSTANTS
EQUATION FOR WATER-GAS SHIFT REACTION, $CO + H_2O \rightleftarrows CO_2 + H$

```
      8
PI= 0.05000     PO= 0.05000
Y=          1.8618       T=      500.0
Y=          1.4975       T=      600.0
Y=          1.2012       T=      700.0
Y=          0.9557       T=      800.0
Y=          0.7490       T=      900.0
Y=          0.5739       T=     1000.0
Y=          0.4237       T=     1100.0
Y=          0.2936       T=     1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


  2    0.1273785E 04    0.1573E 03       0.3566E 00

  1   -0.1867994E 01    0.1834E-01
  2    0.3568009E 04    0.2290E 02       0.9265E-02

  1   -0.2424457E 01    0.6352E-01
  2    0.3912386E 04    0.3967E 02
  3    0.2176132E-03    0.2476E-04       0.2500E-02


  I   A(I)             VARIANCE      STANDARD DEVIATION

  1  -0.2424E 01    0.4035E-02    0.6352E-01
  2   0.3912E 04    0.1574E 04    0.3967E 02
  3   0.2176E-03    0.6134E-09    0.2476E-04
                    0.6250E-05    0.2500E-02

CORRELATION COEFF. ARRAY
 1 1.000-0.996-0.996
 2-0.996 1.000 0.987
 3-0.996 0.987 1.000

COVARIANCE ARRAY
 1 0.403E-02-0.251E 01-0.156E-05
 2-0.251E 01 0.157E 04 0.970E-03
 3-0.156E-05 0.970E-03 0.613E-09

  K   Y OBSERVED   Y COMPUTED     DIFF.       WEIGHTING FACTOR
  1   0.1861E 01   0.1861E 01   0.6158E-03    0.1000E 01
  2   0.1497E 01   0.1498E 01  -0.7214E-03    0.1000E 01
  3   0.1201E 01   0.1201E 01  -0.4093E-03    0.1000E 01
  4   0.9557E 00   0.9555E 00   0.1540E-03    0.1000E 01
  5   0.7490E 00   0.7488E 00   0.1218E-03    0.1000E 01
  6   0.5739E 00   0.5735E 00   0.3907E-03    0.1000E 01
  7   0.4237E 00   0.4234E 00   0.2814E-03    0.1000E 01
  8   0.2936E 00   0.2940E 00  -0.4372E-03    0.1000E 01

VAR. Y= 0.3057E-06
```

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Table 5-5, Part 4. IDEAL GAS EQUILIBRIUM CONSTANTS EQUATION FOR ETHANE HYDROGENATION REACTION, $C_2H_6 + H_2 \rightleftarrows 2CH_4$

```
  4   8
PI= 0.05000     PO= 0.05000
Y=          6.9312      T=      500.0
Y=          6.2986      T=      600.0
Y=          5.7692      T=      700.0
Y=          5.3086      T=      800.0
Y=          4.9274      T=      900.0
Y=          4.5852      T=     1000.0
Y=          4.2908      T=     1100.0
Y=          4.0266      T=     1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


  2    0.6679839E 04   0.6294E 01      0.1426E-01


  1    0.5342789E-01   0.2133E-01
  2    0.6614220E 04   0.2663E 02      0.1077E-01


  1    0.6579201E 00   0.1301E 00
  2    0.6240119E 04   0.8126E 02
  3   -0.2363958E-03   0.5072E-04      0.5120E-02


   I   A(I)            VARIANCE        STANDARD DEVIATION

   1   0.6579E 00      0.1692E-01      0.1301E 00
   2   0.6240E 04      0.6604E 04      0.8126E 02
   3  -0.2363E-03      0.2573E-08      0.5072E-04
                       0.2622E-04      0.5120E-02


CORRELATION COEFF. ARRAY
 1 1.000-0.996-0.996
 2-0.996 1.000 0.987
 3-0.996 0.987 1.000

COVARIANCE ARRAY
 1 0.169E-01-0.105E 02-0.658E-05
 2-0.105E 02 0.660E 04 0.407E-02
 3-0.658E-05 0.407E-02 0.257E-08

  K   Y OBSERVED    Y COMPUTED     DIFF.          WEIGHTING FACTOR
  1   0.6931E 01    0.6933E 01   -0.2216E-02      0.1000E 01
  2   0.6298E 01    0.6296E 01    0.2443E-02      0.1000E 01
  3   0.5769E 01    0.5764E 01    0.4478E-02      0.1000E 01
  4   0.5308E 01    0.5313E 01   -0.5311E-02      0.1000E 01
  5   0.4927E 01    0.4925E 01    0.1464E-02      0.1000E 01
  6   0.4585E 01    0.4587E 01   -0.2679E-02      0.1000E 01
  7   0.4290E 01    0.4290E 01    0.6580E-03      0.1000E 01
  8   0.4026E 01    0.4025E 01    0.1165E-02      0.1000E 01

VAR. Y= 0.1405E-04
```

A7506 1580C

Table 5-5, Part 5. IDEAL GAS EQUILIBRIUM CONSTANTS EQUATION FOR PROPANE HYDROGENATION REACTION, $C_3H_6 + 2H_2 \rightleftarrows 3CH_4$

```
  4   8
PI= 0.05000      PO= 0.05000
Y=          13.0618        T=      500.0
Y=          11.8679        T=      600.0
Y=          10.8688        T=      700.0
Y=          10.0229        T=      800.0
Y=           9.2911        T=      900.0
Y=           8.6478        T=     1000.0
Y=           8.0812        T=     1100.0
Y=           7.5849        T=     1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


  2     0.1259091E 05    0.1264E 02       0.2865E-01


   I    A(I)             VARIANCE         STANDARD DEVIATION

   2    0.1259E 05       0.1598E 03       0.1264E 02
                         0.8209E-03       0.2865E-01

CORRELATION COEFF. ARRAY
 2 1.000

COVARIANCE ARRAY
 2 0.159E 03

  K    Y OBSERVED     Y COMPUTED      DIFF.          WEIGHTING FACTOR
  1    0.1306E 02     0.1312E 02    -0.5824E-01      0.1000E 01
  2    0.1186E 02     0.1188E 02    -0.1401E-01      0.1000E 01
  3    0.1086E 02     0.1085E 02     0.1147E-01      0.1000E 01
  4    0.1002E 02     0.9995E 01     0.2749E-01      0.1000E 01
  5    0.9291E 01     0.9260E 01     0.3083E-01      0.1000E 01
  6    0.8647E 01     0.8625E 01     0.2193E-01      0.1000E 01
  7    0.8081E 01     0.8072E 01     0.8398E-02      0.1000E 01
  8    0.7584E 01     0.7586E 01    -0.1492E-02      0.1000E 01

VAR. Y= 0.8544E-03
```

A7506 1580D

Table 5-5, Part 6. IDEAL GAS HEATS OF REACTION EQUATION FOR METHANATION REACTION, $CO + 3H_2 \rightleftarrows CH_4 + H_2O$

```
PAGE   2    TEMP           INI

      SUBROUTINE INLC5(X,WT)
C     DEFINE X ARRAY AND WEIGHT  (WT)
C     SET X(NP+1) = DEPENDENT VARIABLE
C         **********
      DIMENSION X(31)
      IOUT = 5
      READ (2,10) Y,T
      WRITE (IOUT,900) Y,T
      T=T+459.67
      X(1)=1.
      X(2)=T
      X(3)=T*T
      X(4)=T*T*T
      X(5)=Y
      WT=1.0
      RETURN
   10 FORMAT (F15.4,F10.1)
  900 FORMAT (3H Y=F15.4,6X,2HT=F10.1)
      END
VARIABLE ALLOCATIONS
     Y(R )=0000          T(R )=0002       IOUT(I )=0004

STATEMENT ALLOCATIONS
 10   =0010  900  =0013

FEATURES SUPPORTED
 ONE WORD INTEGERS

CALLED SUBPROGRAMS
 FADD    FMPY    FLD     FSTO    FSTUX   SRED    SWRT    SCOMP   SIOF    SUBIN

REAL CONSTANTS
  .459670E 03=000A    .100000E 01=000C

INTEGER CONSTANTS
     5=000E      2=000F

CORE REQUIREMENTS FOR INLC5
 COMMON      0  VARIABLES     10  PROGRAM     96

RELATIVE ENTRY POINT ADDRESS IS 001C (HEX)

END OF COMPILATION

// DUP

*STORE      WS  UA  INLC5
CART ID 0001   DB ADDR  4835   DB CNT   0008

// XEQ LRMC5
```

A7506 1580E

Table 5-5, Part 7. IDEAL GAS HEATS OF REACTION EQUATION FOR WATER-GAS SHIFT REACTION, $CO + H_2O \rightleftarrows CO_2 + H_2$

```
  4   8
PI= 0.05000     PO= 0.05000
Y=    -92804.0158       T=     500.0
Y=    -93566.0158       T=     600.0
Y=    -94252.0158       T=     700.0
Y=    -94863.0158       T=     800.0
Y=    -95404.0158       T=     900.0
Y=    -95880.0158       T=    1000.0
Y=    -96283.0158       T=    1100.0
Y=    -96628.0158       T=    1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


  1   -0.9496001E 05   0.4752E 03      0.1344E 04


  1   -0.8782337E 05   0.3505E 03
  2   -0.5449179E 01   0.2636E 00      0.1708E 03


   I   A(I)           VARIANCE      STANDARD DEVIATION

   1  -0.8782E 05    0.1228E 06    0.3505E 03
   2  -0.5449E 01    0.6951E-01    0.2636E 00
                     0.2919E 05    0.1708E 03

CORRELATION COEFF. ARRAY
 1 1.000-0.985
 2-0.985 1.000

COVARIANCE ARRAY
 1 0.122E 06-0.910E 02
 2-0.910E 02 0.695E-01

  K    Y OBSERVED    Y COMPUTED     DIFF.        WEIGHTING FACTOR
  1   -0.9280E 05   -0.9305E 05    0.2487E 03    0.1000E 01
  2   -0.9356E 05   -0.9359E 05    0.3168E 02    0.1000E 01
  3   -0.9425E 05   -0.9414E 05   -0.1094E 03    0.1000E 01
  4   -0.9486E 05   -0.9468E 05   -0.1754E 03    0.1000E 01
  5   -0.9540E 05   -0.9523E 05   -0.1715E 03    0.1000E 01
  6   -0.9588E 05   -0.9577E 05   -0.1026E 03    0.1000E 01
  7   -0.9628E 05   -0.9632E 05    0.3926E 02    0.1000E 01
  8   -0.9662E 05   -0.9686E 05    0.2391E 03    0.1000E 01

VAR. Y= 0.3406E 05
```

A7506 1580F

Table 5-5, Part 8. IDEAL GAS HEATS OF REACTION EQUATION FOR WATER-GAS SHIFT REACTION, $CO + H_2O \rightleftharpoons CO_2 + H_2$

```
  4   8
PI= 0.05000     PO= 0.05000
Y=    -17006.0039      T=     500.0
Y=    -16777.0039      T=     600.0
Y=    -16538.0039      T=     700.0
Y=    -16293.0019      T=     800.0
Y=    -16044.0019      T=     900.0
Y=    -15787.0019      T=    1000.0
Y=    -15544.0019      T=    1100.0
Y=    -15299.0019      T=    1200.0


TERMS CONSIDERED   1  2  3  4
TERMS FORCED IN    0


  1   -0.1616100E 05   0.2125E 03      0.6011E 03


  1   -0.1780901E 05   0.4627E 02
  3    0.9322765E-03   0.2478E-04      0.4218E 02


   I   A(I)          VARIANCE      STANDARD DEVIATION

   1  -0.1780E 05    0.2141E 04    0.4627E 02
   3   0.9322E-03    0.6140E-09    0.2478E-04
                     0.1779E 04    0.4218E 02

CORRELATION COEFF. ARRAY
 1 1.000-0.946
 3-0.946 1.000

COVARIANCE ARRAY
 1 0.214E 04-0.108E-02
 3-0.108E-02 0.614E-09

  K   Y OBSERVED   Y COMPUTED    DIFF.       WEIGHTING FACTOR
  1  -0.1700E 05  -0.1695E 05  -0.5558E 02   0.1000E 01
  2  -0.1677E 05  -0.1676E 05  -0.1483E 02   0.1000E 01
  3  -0.1653E 05  -0.1655E 05   0.1725E 02   0.1000E 01
  4  -0.1629E 05  -0.1632E 05   0.3670E 02   0.1000E 01
  5  -0.1604E 05  -0.1608E 05   0.4151E 02   0.1000E 01
  6  -0.1578E 05  -0.1582E 05   0.3567E 02   0.1000E 01
  7  -0.1554E 05  -0.1554E 05  -0.2812E 01   0.1000E 01
  8  -0.1529E 05  -0.1524E 05  -0.5794E 02   0.1000E 01

VAR. Y= 0.1886E 04
```

A7506 1580G

Table 5-5, Part 9. IDEAL HAS HEATS OF REACTIONS EQUATION FOR ETHANE HYDROGENATION REACTION, $C_2H_6 + H_2 \rightleftharpoons 2CH_4$

```
  4   8
PI= 0.05000     PO= 0.05000
Y=     -29301.0039        T=      500.0
Y=     -29637.0039        T=      600.0
Y=     -29969.0039        T=      700.0
Y=     -30287.0039        T=      800.0
Y=     -30580.0039        T=      900.0
Y=     -30858.0039        T=     1000.0
Y=     -31120.0039        T=     1100.0
Y=     -31354.0039        T=     1200.0


TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0


  1   -0.3038825E 05   0.2555E 03      0.7226E 03


  1   -0.2653019E 05   0.8844E 02
  2   -0.2945827E 01   0.6652E-01      0.4311E 02


  I   A(I)            VARIANCE        STANDARD DEVIATION

  1  -0.2653E 05   0.7822E 04   0.8844E 02
  2  -0.2945E 01   0.4424E-02   0.6652E-01
                   0.1858E 04   0.4311E 02

CORRELATION COEFF. ARRAY
 1 1.000-0.985
 2-0.985 1.000

COVARIANCE ARRAY
 1 0.782E 04-0.579E 01
 2-0.579E 01 0.442E-02

  K   Y OBSERVED    Y COMPUTED     DIFF.        WEIGHTING FACTOR
  1  -0.2930E 05  -0.2935E 05   0.5620E 02   0.1000E 01
  2  -0.2963E 05  -0.2965E 05   0.1478E 02   0.1000E 01
  3  -0.2996E 05  -0.2994E 05  -0.2262E 02   0.1000E 01
  4  -0.3028E 05  -0.3024E 05  -0.4604E 02   0.1000E 01
  5  -0.3058E 05  -0.3053E 05  -0.4446E 02   0.1000E 01
  6  -0.3085E 05  -0.3083E 05  -0.2787E 02   0.1000E 01
  7  -0.3112E 05  -0.3112E 05   0.4703E 01   0.1000E 01
  8  -0.3135E 05  -0.3141E 05   0.6528E 02   0.1000E 01

VAR. Y= 0.2174E 04
```

A7506 1580H

Table 5-5, Part 10. IDEAL GAS HEATS OF REACTIONS EQUATION FOR PROPANE HYDROGENATION REACTION, $C_3H_8 + 2H_2 \rightleftharpoons 3CH_4$

```
  4   8
PI= 0.05000     PU= 0.05000
Y=     -54953.0079        T=      500.0
Y=     -55686.0079        T=      600.0
Y=     -56405.0079        T=      700.0
Y=     -57089.0079        T=      800.0
Y=     -57743.0079        T=      900.0
Y=     -58353.0079        T=     1000.0
Y=     -58924.0079        T=     1100.0
Y=     -59445.0079        T=     1200.0



TERMS CONSIDERED   1   2   3   4
TERMS FORCED IN    0



  1   -0.5732475E 05   0.5588E 03      0.1580E 04


  1   -0.4888546E 05   0.1822E 03
  2   -0.6443833E 01   0.1370E 00      0.8884E 02


   I   A(I)           VARIANCE      STANDARD DEVIATION

   1  -0.4888E 05    0.3322E 05    0.1822E 03
   2  -0.6443E 01    0.1879E-01    0.1370E 00
                     0.7892E 04    0.8884E 02

CORRELATION COEFF. ARRAY
 1 1.000-0.985
 2-0.985 1.000

COVARIANCE ARRAY
 1 0.332E 05-0.246E 02
 2-0.246E 02 0.187E-01

  K    Y OBSERVED    Y COMPUTED     DIFF.        WEIGHTING FACTOR
  1  -0.5495E 05   -0.5506E 05   0.1163E 03    0.1000E 01
  2  -0.5568E 05   -0.5571E 05   0.2778E 02    0.1000E 01
  3  -0.5640E 05   -0.5635E 05  -0.4683E 02    0.1000E 01
  4  -0.5708E 05   -0.5700E 05  -0.8644E 02    0.1000E 01
  5  -0.5774E 05   -0.5764E 05  -0.9606E 02    0.1000E 01
  6  -0.5835E 05   -0.5829E 05  -0.6167E 02    0.1000E 01
  7  -0.5892E 05   -0.5893E 05   0.1170E 02    0.1000E 01
  8  -0.5944E 05   -0.5958E 05   0.1350E 03    0.1000E 01

VAR. Y= 0.9234E 04
```

A7506 1580I

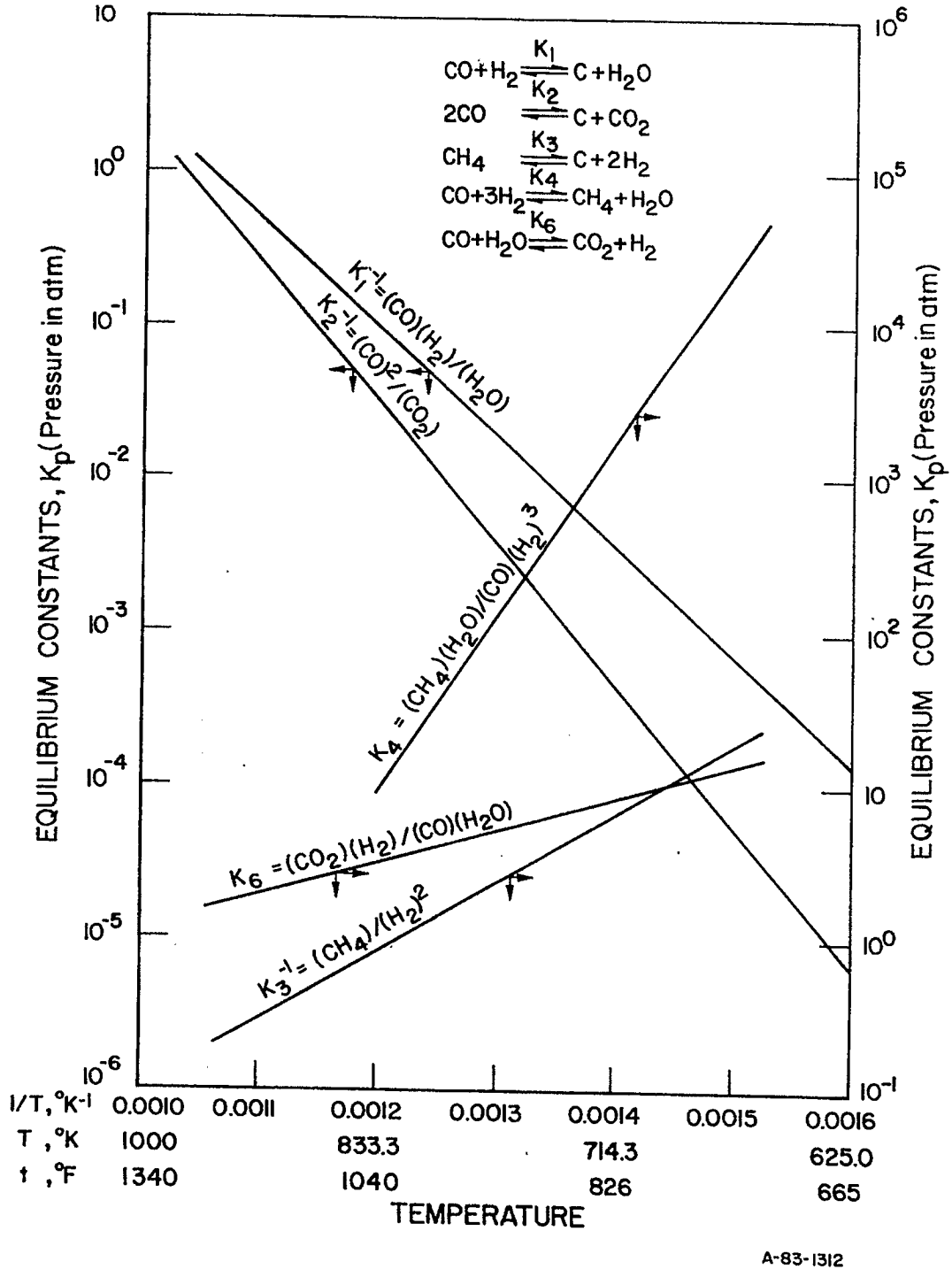

Figure 5-14. EQUILIBRIUM CONSTANTS AS A FUNCTION OF TEMPERATURE

Table 5-6. ANALYSIS OF PRODUCT COMPONENTS IN METHANATION FOR COAL GASIFICATION

α_1 = number of moles of CO reacted from Equation 1

α_2 = number of moles of CO reacted from Equation 2

α_3 = number of moles of C_2H_6 reacted from Equation 4

α_4 = number of moles of C_3H_8 reacted from Equation 5

Total number of moles in feed = $N = (CO) + (H_2) + (CH_4) + (CO_2) + (H_2O) + (C_2H_6) + (C_3H_8)$

moles of CO in product = $(CO) - \alpha_1 - \alpha_2$

moles of H_2 in product = $(H_2) - 3\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4$

moles of CH_4 in product = $(CH_4) + \alpha_1 + 2\alpha_3 + 3\alpha_4$

moles of CO_2 in product = $(CO_2) + \alpha_2$

moles of H_2O in product = $(H_2O) + \alpha_1 - \alpha_2$

moles of C_2H_6 in product = $(C_2H_6) - \alpha_3$

moles of C_3H_8 in product = $(C_3H_8) - \alpha_4$

total number of moles in product = $N - 2\alpha_1$

$$K_1 = \frac{[(CH_4) + \alpha_1 + 2\alpha_3 + 3\alpha_4][(H_2O) + \alpha_1 - \alpha_2][N - 2\alpha_1]^2}{[(CO) - \alpha_1 - \alpha_2][(H_2) - 3\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4]^3 \quad p^2} \tag{9}$$

$$K_2 = \frac{[(CO_2) + \alpha_2][(H_2) - 3\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4]}{[(CO) - \alpha_1 - \alpha_2][(H_2O + \alpha_1 - \alpha_2]} \tag{10}$$

$$K_4 = \frac{[(CH_4) + \alpha_1 + 2\alpha_3 + 3\alpha_4]^2}{[(C_2H_6) - \alpha_3][(H_2) - 3\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4]} \tag{11}$$

$$K_5 = \frac{[(CH_4) + \alpha_1 + 2\alpha_3 + 3\alpha_4]^3}{[(C_3H_8) - \alpha_4][(H_2) - 3\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4]} \tag{12}$$

A7506 1581

Table 5-7, Part 1. SOLUTIONS OF SIMULTANEOUS REACTIONS IN METHANATION FOR COAL GASIFICATION

```
PAGE   1

// JOB

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0001        0001        0000
                          2801        0001
                          2603        0002

V2 M11   ACTUAL 16K  CONFIG 16K

// FOR
*ONE WORD INTEGERS
*EXTENDED PRECISION
*LIST SOURCE PROGRAM
      SUBROUTINE OUTIE
      INTEGER OUT
      DIMENSION Y(16),Z(16)
      COMMON X(30),A(40),F(30),W(30,31),M,M1,N
      OUT=5
      F(9)=X(1)
      F(10)=X(2)
      F(11)=X(3)
      F(12)=X(4)
      Y(9)=A(1)
      Y(10)=A(2)
      Y(11)=A(3)
      Y(12)=A(4)
      Y(13)=A(5)
      Y(14)=A(6)
      Y(15)=0.0
      Z(9)=A(1)-X(1)-X(2)
      Z(10)=A(2)-3.*X(1)+X(2)-X(3)-2.*X(4)
      Z(11)=A(3)+X(1)+2.*X(3)+3.*X(4)
      Z(12)=A(4)+X(2)
      Z(13)=A(5)-X(3)
      Z(14)=A(6)-X(4)
      Z(15)=X(1)-X(2)
      P=1000.
      T=A(7)+459.67
      X(9)=EXP(2.302585*(-11.61675+19914.35/T-0.4894912*T/1000.))
      X(10)=EXP(2.302585*(-2.424457+3912.386/T+0.2176132*T/1000.))
      X(11)=EXP(2.302585*(0.6579201+6240.119/T-0.2363958*T/1000.))
      X(12)=EXP(2.302585*(1.536+11570./T-0.5604*T/1000.))
      A(9)=-80791.37-393.0441*T**.5
      A(10)=-22508.69+176.0879*T**.5
      A(11)=-26530.19-2.945827*T
      A(12)=-48885.46-6.443833*T
      WRITE (OUT,1000)
 1000 FORMAT('     P'113'T'T29'K'T49'H'T67'ALPHA'T88'YIN'T107'YOUT')
      WRITE (OUT,10)P,A(7),(X(I),A(I),F(I),Y(I),Z(I),I=9,12),(Y(I),Z(I),
     1I=13,15)
   10 FORMAT (F7.0,F8.0,5E20.7,/,3(15X,5E20.7,/),3(75X,2E20.7,/))
      RETURN
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 EXTENDED PRECISION
```

A7506 1582

Table 5-7, Part 2. SOLUTIONS OF SIMULTANEOUS REACTIONS IN METHANATION FOR COAL GASIFICATION

```
PAGE   2

CORE REQUIREMENTS FOR OUTIE
 COMMON   3094  VARIABLES    128  PROGRAM    606

RELATIVE ENTRY POINT ADDRESS IS 0103 (HEX)

END OF COMPILATION

// DUP

*DELETE        OUTIE
CART ID 0001   DB ADDR  4A65   DB CNT   002C

*STORE      WS  UA  OUTIE
CART ID 0001   DB ADDR  4A65   DB CNT   002D

PAGE   1

// JOB                                                          1

LOG DRIVE   CART SPEC   CART AVAIL   PHY DRIVE
  0000        0001        0001         0000
                          2801         0001
                          2603         0002

V2 M11   ACTUAL 16K  CONFIG 16K

*EQUAT(OUTC7,OUTIE)

// FOR
*ONE WORD INTEGERS
*EXTENDED PRECISION
*LIST SOURCE PROGRAM
**    SUBROUTINE FXNC7,USE WITH SEQC7 TO COMPUTE SIMULT. EQUATIONS
```

A7506 1582A

Table 5-7, Part 3. SOLUTIONS OF SIMULTANEOUS REACTIONS IN METHANATION FOR COAL GASIFICATION

```
PAGE   2                    SUBROUTINE FXNC7,USE WITH SEQC7 TO COMPUTE SIMULT. EQUATIONS

      SUBROUTINE FXNC7
C       ***********
C     DO NOT CHANGE ANY VARIABLES IN COMMON,EXCEPT  F  ARRAY
C     FIRST EQUATION = F(1) = 0.0
C     SECOND EQUATION = F(2) = 0.0
C     M       EQUATION = F(M) = 0.0
C       ***********
      COMMON X(30),A(40),F(30)
      T=A(7)+459.67              °R
      RK1=EXP(2.302585*(-11.61675+19914.35/T-0.4894912*T/1000.))
      RK2=EXP(2.302585*(-2.424457+3912.386/T+0.2176132*T/1000.))
      RK3=EXP(2.302585*(0.6579201+6240.119/T-0.2363958*T/1000.))
      RK4=EXP(2.302585*(1.536+11570./T-0.5604*T/1000.))
      F(1)=(A(3)+X(1)+2.*X(3)+3.*X(4))*(X(1)-X(2))*(100.-2.*X(1))**2-((A
     1(1)-X(1)-X(2))*(A(2)-3.*X(1)+X(2)-X(3)-2.*X(4))**3*68.*68.)*RK1
      F(2)=(A(4)+X(2))*(A(2)-3.*X(1)+X(2)-X(3)-2.*X(4))-((A(1)-X(1)-X(2)
     1)*(X(1)-X(2)))*RK2
      F(3)=(A(3)+X(1)+2.*X(3)+3.*X(4))**2-((A(5)-X(3))*(A(2)-3.*X(1)+X(2
     1)-X(3)-2.*X(4)))*RK3
      F(4)=(A(3)+X(1)+2.*X(3)+3.*X(4))**3-((A(6)-X(4))*(A(2)-3.*X(1)+X(2
     1)-X(3)-2.*X(4))**2)*RK4
      RETURN
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 EXTENDED PRECISION

CORE REQUIREMENTS FOR FXNC7
 COMMON     300  VARIABLES      44  PROGRAM     512

RELATIVE ENTRY POINT ADDRESS IS 0067 (HEX)

END OF COMPILATION

// DUP

*DELETE              FXNC7
CART ID 0001   DB ADDR  4A10   DB CNT   0028

*STORE      WS  UA  FXNC7
CART ID 0001   DB ADDR  4A6A   DB CNT   0028

// XEQ SEQC7
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Table 5-8. IDEAL GAS EQUILIBRIUM COMPOSITIONS FOR METHANATION OF TYPICAL HYGAS PRODUCTS AT 1000 psia

Feed Gas Composition, mol %		Temperature, °F / Product Gas Composition, mol %	500	750	1000
HIGH-CO FEED					
CO	10.3	CO	0.01	0.04	0.55
H_2	31.2	H_2	2.69	1.49	5.34
CH_4	55.7	CH_4	82.49	83.25	80.30
CO_2	2.3	CO_2	3.64	3.34	3.84
C_2H_6	0.3	C_2H_6	--	0.01	0.03
C_3H_8	0.2	C_3H_8	--	--	--
Total	100.0	H_2O	11.17	11.87	9.94
		Total	100.00	100.00	100.00
INTERMEDIATE-CO FEED					
CO	6.6	CO	0.00	0.03	0.49
H_2	23.6	H_2	--	1.47	5.05
CH_4	67.0	CH_4	88.45	87.56	84.72
CO_2	2.3	CO_2	1.53	2.09	2.60
C_2H_6	0.4	C_2H_6	--	0.01	0.04
C_3H_8	0.1	C_3H_8	--	--	--
Total	100.0	H_2O	10.02	8.84	7.10
		Total	100.00	100.00	100.00
LOW-CO FEED					
CO	2.4	CO	0.00	0.03	0.56
H_2	11.1	H_2	--	1.09	3.58
CH_4	84.1	CH_4	93.19	93.80	91.61
CO_2	1.8	CO_2	--	1.34	1.54
C_2H_6	0.4	C_2H_6	--	0.02	0.06
C_3H_8	0.2	C_3H_8	--	--	0.00
Total	100.0	H_2O	6.81	3.72	2.65
		Total	100.00	100.00	100.00

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Table 5-9. SOME PHYSICAL PROPERTIES OF METAL CARBONYLS

Metal Carbonyl	Color and State	m. p; °C	b. p; °C	Vapor Pressure	Specific Gravity	Temperature of Formation °C	Decomposition
$Ni(CO)_4$	water-clear liquid	-25^0	43^0	$238mm^{15^0}$	1.310	$30-50^0$	To CO and Ni at 1 atm. and 50^0 C
$Co_2(CO)_8$	orange crystals	51^0	decomp. ca. 52^0	$0.72mm^{15^0}$	1.73	220^0 at 150 atm	To CO and Co at 1 atm. above 60^0 C
$Fe(CO)_5$	water-clear liquid	19.5^0	104.6^0	$25.9mm^{15^0}$	1.453	173^0 at 200 atm.	To CO and Fe above 130^0 C (1 atm)
$Fe_2(CO)_9$	gold hexagonal plates	decomposed ca. 100^0		--	2.085	action of light on $Fe(CO)_3$ at ambient temp.	--
$Fe_3(CO)_{12}$	dark green tablets	decomposed at $140-150^0$		--	1.996	--	To Fe and CO at 150^0 C
$Cr(CO)_6$	colorless orthorhombic crystals	Sublimes at room temperature		$60.6mm^{100^0}$	--	$0-4^0$	To CO and Cr by light and at 200^0 C
$Mo(CO)_6$	colorless crystals	Sublimes at $30-40^0$		$43.2mm^{100^0}$	1.96	200^0 at 200 atm.	To Co and Mo above 150^0 C
$W(CO)_6$	colorless crystals	Sublimes at 50^0		$14.4mm^{100^0}$	--	$0-4^0$	To CO and W above 100^0 C

The vapor density of all the carbonyls is several times greater than air.

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where the catalyst failed. The feed gas used for the test was one or all three of the compositions listed in Table 5-8 for the initial activity test. The feed gas composition was varied for the subsequent tests to fit the specific purposes. Fresh catalyst was used for each new step and the test always began with step 1. For example, fresh catalyst was loaded for study of the high-temperature limit. It was first tested for activity as in step 1, then followed by the scheduled test. If the activity test differed greatly with the initial step 1 test, a new batch of catalyst was loaded. The testing was very time consuming, because it involved careful assembling and disassembling, heat-up, cool-down and pressure-testing of the equipment, as well as pretreatment, aftertreatment and analysis of the catalyst. The deactivated catalyst was analyzed for the changes in crushing strength, carbon content, sulfur content, metal content, crystal structure and surface area. If a catalyst was under secrecy agreement, it was sent back to the catalyst manufacturer for the above analyses and the findings were required to be reported to HYGAS investigators. The catalysts were compared for physical strength, activity, temperature limits, resistance to potential poisons and deactivation behavior. (The suitability of a catalyst or catalysts depends on the coal gasification process used. If the design information for the methanator is known, it is possible to recommend the most suitable catalysts for the operation based on the experience gained at the Chicago laboratories of the HYGAS researchers.)

5.5.2 Temperature Stability

Because the methanation reaction is very exothermic, there was always concern that the catalyst bed temperature could exceed the calculated adiabatic equilibrium temperature at some operating conditions. To study these "hot spots", investigators mounted the catalyst in a stationary basket as shown in Figure 5-5. Thermocouples were inserted into the catalyst pellets. Typical temperature gradients between the catalyst and bulk gas are presented in Table 5-10. These data indicate that heat transfer effects were minimal over the range of conditions expected for HYGAS operation. Higher values of feed gas rate, mole percent carbon monoxide in the feed, and percent conversion of carbon monoxide cause the higher temperature gradients as expected.

5.5.3 Screening Tests of Commercial Methanation Catalysts

The first batch of catalysts selected for coal gasification methanation test were Harshaw Ni-0104T (nickel on kieselguhr), Catalyst and Chemicals C-13-4 (nickel on alumina), Girdler G-65 (nickel on alumina), and Engelhard 12468 (ruthenium on alumina). These catalysts were tested for temperatures from 485° to 1000°F at 1000 psig. The results are presented in Tables 5-11 to 5-16. (Table 5-11 gives the data from the CSTR Blank runs.) The initial test results showed that:

- Harshaw Ni-0104T is the most active, perhaps due to the highest nickel content. It is the weakest physically and has an effective temperature range of 550° to 900°F. It will operate at 525° and 960°F, but at reduced activity level and may deactivate rapidly if prolonged use is maintained at these temperature limits.

Table 5-10. TYPICAL TEMPERATURE GRADIENTS BETWEEN CATALYST AND BULK GAS FOR HYGAS METHANATION

Feed Rate, SCF/hr	Mole % CO in Feed Gas	CO Conv, %	$T_{cat.} - T_{gas}$, °F
4.50	2.4	65.2	2
5.96	2.4	53.4	2
9.62	2.4	40.7	2
6.47	7.0	36.6	1
7.20	7.0	33.3	2
8.80	7.0	28.6	3
3.90	10.0	50.5	2
7.20	10.0	33.4	3
9.70	10.0	31.3	9
9.94	10.0	22.8	7
11.31	10.0	24.5	11

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Table 5-11. METHANATION DATA - CSTR BLANK RUNS

Run Number	62	63	64	323	324	325*
Catalyst Weight, g	0.0	0.0	0.0	0.0	0.0	0.0
Feed Gas Rate, SCF/hr	4.29	3.67	3.21	4.33	8.19	8.09
Feed Gas Composition, mole %						
Nitrogen	1.4	1.4	1.4	--	--	--
Helium	0.0	0.0	0.0	--	0.3	0.3
Carbon Monoxide	1.5	1.5	1.5	42.1	43.4	43.5
Carbon Dioxide	0.3	0.3	0.3	0.1	0.1	0.1
Hydrogen	47.7	47.7	47.7	57.4	56.1	56.0
Methane	46.4	46.4	46.3	0.0	0.0	0.0
Ethane	2.1	2.1	2.1	0.3	0.1	0.1
Propane	0.6	0.6	0.6	0.1	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, ^{0}F	790	900	1010	1118	1125	1323
Reactor Pressure, psig	1000	1000	1000	585	300	325
Product Gas Rate, SCF/hr	4.29	3.67	3.11	3.86	6.88	6.59
Product Gas Composition, mole %						
Nitrogen	1.4	1.4	1.4	--	--	--
Helium	0.0	0.0	0.0	--	0.5	0.5
Carbon Monoxide	1.7	1.8	1.8	40.3	41.1	40.0
Carbon Dioxide	0.2	0.1	0.1	3.1	0.9	1.9
Hydrogen	47.6	47.7	47.4	52.7	56.2	54.7
Methane	46.4	46.3	46.6	3.2	1.2	2.7
Ethane	2.1	2.1	2.2	0.6	0.1	0.2
Propane	0.6	0.6	0.5	0.1	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	31.8	31.8	31.8	1.36	1.29	1.29
Water Collected, lb/hr x 10^4	0.0	0.0	0.0	0.0	0.0	0.0
% CO Converted	0.0	0.0	0.0	14	20	25

*Carbon deposition reaction detected.

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Table 5-12. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Catalyst Weight, g	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64	19.64
Feed Gas Rate, SCF/hr	10.0	16.7	19.7	10.0	12.5	21.5	24.1	29.1	21.5	12.8	6.75	10.3	12.7	12.6	12.1
Feed Gas Composition, mole %															
Helium	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.6	0.6	0.6	0.6
Carbon Monoxide	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	2.1	6.2	6.2	6.2	6.2
Carbon Dioxide	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.8	1.8	1.8	1.8
Hydrogen	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	11.7	26.3	26.3	26.3	26.3
Methane	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	83.0	64.5	64.5	64.5	64.5
Ethane	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.4	0.4	0.4	0.4
Propane	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	560	560	560	560	560	560	560	560	560	560	560	560	560	560	560
Reactor Pressure, psig	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	8.68	15.0	18.1	8.65	11.0	20.1	22.5	26.9	20.3	11.3	3.98	7.90	10.6	10.3	11.0
Product Gas Composition, mole %															
Helium	0.4	0.4	0.4	0.5	0.4	0.4	0.4	0.5	0.5	0.4	0.4	1.0	0.8	0.8	0.8
Carbon Monoxide	0.1	0.4	0.5	0.2	0.3	1.2	0.7	0.8	0.7	0.4	0.1	1.0	1.7	1.8	0.3
Carbon Dioxide	1.3	1.4	1.4	1.4	1.4	1.5	1.4	1.5	1.4	1.3	1.3	1.9	1.8	1.8	1.3
Hydrogen	1.8	3.0	3.4	1.7	1.9	5.1	4.1	4.6	3.9	2.4	1.1	4.9	6.1	6.3	2.6
Methane	95.8	94.0	93.7	95.6	95.5	91.3	92.8	92.0	92.9	95.0	96.7	90.6	89.5	89.3	94.7
Ethane	0.5	0.6	0.6	0.6	0.5	0.5	0.6	0.6	0.6	0.5	0.6	0.5	0.1	0.0	0.3
Propane	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	5.57	5.57	5.57	5.57	5.57	5.57	5.57	5.57	5.57	5.57	5.57	4.24	4.24	4.24	4.24
Water Collected, lb/hr x 10^4	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Rate of Methane Formation, lb-mole/hr-g catalyst x 10^4	0.25	0.52	0.80	0.25	0.17	0.67	1.16	0.79	1.34	0.15	0.18	0.68	1.71	1.42	3.45

Table 5-13. METHANATION DATA - CATALYST EVALUATION (CCI C-13-4)

Data Number	16	17
Catalyst Weight,	7.81	7.81
Feed Gas Rate, SCF/hr	7.35	5.85
Feed Gas Composition, mole		
Helium	0.0	0.0
Carbon Monoxide	10.5	10.5
Carbon Dioxide	2.7	2.7
Hydrogen	32.6	32.6
Methane	53.8	53.8
Ethane	0.3	0.3
Propane	0.1	0.1
Total	100.0	100.0
Reactor Temperature, ^{0}F	700	700
Reactor Pressure, psi	1000	1000
Product Gas Rate, SCF/hr	7.01	5.45
Product Gas Composition, mole		
Helium	0.0	0.0
Carbon Monoxide	9.75	2.19
Carbon Dioxide	2.33	1.70
Hydrogen	30.2	10.3
Methane	57.22	85.3
Ethane	0.4	0.3
Propane	0.1	0.1
Total	100.00	100.00
Feed Ha/CO Ratio	3.10	3.10
Water Collected, lt/hr x 10^4	--	--
Rate of Methane Formation, lb mole/hr-catalyst x 10^4	0.20	4.99

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Table 5-14. METHANATION DATA - CATALYST EVALUATION (Girdler G-65)

Run Number	18	19	20	21	22
Catalyst Weight, g	27.3	27.3	27.3	27.3	27.3
Feed Gas Rate, SCF/hr	10.8	10.8	5.83	5.83	5.83
Feed Gas Composition, mole %					
Helium	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	10.5	10.5	10.5	10.5	10.5
Carbon Dioxide	2.7	2.7	2.7	2.7	2.7
Hydrogen	32.6	32.6	32.6	32.6	32.6
Methane	53.8	53.8	53.8	53.8	53.8
Ethane	0.3	0.3	0.3	0.3	0.3
Propane	0.1	0.1	0.1	0.1	0.1
Total	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, ^{0}F	720	720	770	820	900
Reactor Pressure, psig	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	9.48	8.76	4.13	3.99	3.71
Product Gas Composition, mole %					
Helium	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	6.95	6.85	4.34	3.80	3.00
Carbon Dioxide	2.74	2.58	2.83	2.78	2.73
Hydrogen	21.8	21.47	14.4	10.8	10.6
Methane	68.21	68.7	78.0	82.5	83.3
Ethane	0.3	0.4	0.43	0.12	0.37
Propane	0.0	0.0	0.0	0.0	0.0
Total	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO Ratio	3.10	3.10	3.10	3.10	3.10
Water Collected, lb/hr x 10^4	--	--	--	--	--
Rate of Methane Formation, lb mole/hr-g catalyst x 10^4	0.62	0.20	0.41	0.44	0.48

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Table 5-15. METHANATION DATA - CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	23	24	25	26	27	28	29	30
Catalyst Weight, g	28.05	28.05	28.05	28.05	28.05	28.05	28.05	28.05
Feed Gas Rate, SCF/hr	6.40	6.40	6.40	6.40	6.40	6.40	6.62	6.62
Feed Gas Composition, mole %								
Nitrogen	0.11	0.11	0.11	0.11	0.11	0.11	0.35	0.35
Carbon Monoxide	10.3	10.3	10.3	10.3	10.3	10.3	6.90	6.90
Carbon Dioxide	2.33	2.33	2.33	2.33	2.33	2.33	1.98	1.98
Hydrogen	31.2	31.2	31.2	31.2	31.2	31.2	23.2	23.2
Methane	55.7	55.7	55.7	55.7	55.7	55.7	66.9	66.9
Ethane	0.26	0.26	0.26	0.26	0.26	0.26	0.37	0.37
Propane	0.10	0.10	0.10	0.10	0.10	0.10	0.30	0.30
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	615	615	700	800	800	900	900	800
Reactor Pressure, psig	1000	1000	1000	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	4.52	4.53	4.47	4.48	3.70	3.63	4.39	4.92
Product Gas Composition, mole %								
Nitrogen	0.16	0.16	0.16	0.16	0.19	0.19	0.53	0.47
Carbon Monoxide	0.44	0.60	0.32	0.39	0.39	0.48	0.41	0.32
Carbon Dioxide	3.01	3.00	3.09	3.28	3.22	3.25	2.40	2.20
Hydrogen	2.66	3.04	2.73	3.27	3.30	5.08	4.30	2.90
Methane	93.6	93.1	93.7	92.9	92.9	91.0	92.3	94.1
Ethane	0.1	0.07	0.0	0.0	0.0	0.0	0.06	0.01
Propane	0.03	0.03	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO Ratio	3.03	3.03	3.03	3.03	3.03	3.03	3.36	3.36
Water Collected, lb/hr x 10^4	--	--	--	--	--	--	--	--
Rate of Methane Formation, lb-mole/hr-g catalyst x 10^4	0.62	0.60	1.18	0.55	0.47	0.45	0.41	0.41

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Table 5-16. METHANATION DATA - CATALYST EVALUATION
(Engelhard 12468)

Run Number	31	32	33
Catalyst Weight, g	10.33	10.33	10.33
Feed Gas Rate, SCF/hr	--	--	--
Feed Gas Composition, mole %			
Nitrogen	0.35	0.35	0.35
Carbon Monoxide	6.90	6.90	6.90
Carbon Dioxide	1.98	1.98	1.98
Hydrogen	23.2	23.2	23.2
Methane	66.9	66.9	66.9
Ethane	0.37	0.37	0.37
Propane	0.30	0.30	0.30
Total	100.00	100.00	100.00
Reactor Temperature, ^{0}F	485	600	670
Reactor Pressure, psig	1000	1000	1000
Product Gas Rate, SCF/hr	5.40	4.81	4.32
Product Gas Composition, mole %			
Nitrogen	0.35	0.23	0.41
Carbon Monoxide	6.53	4.18	0.89
Carbon Dioxide	2.03	2.21	2.31
Hydrogen	13.0	15.9	6.53
Methane	77.1	76.7	89.2
Ethane	0.68	0.61	0.51
Propane	0.31	0.17	0.15
Total	100.00	100.00	100.00
Feed H_2/CO Ratio	3.36	3.36	3.36
Water Collected, lb/hr x 10^4	--	--	--
Rate of Methane Formation, lb mole/hr-g catalyst x 10^4	--	--	--

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• Girdler G-65 is the strongest physically but has the lowest activity. It has poor low-temperature activity (600°F) but good high-temperature limit (1000°). The upper temperature limit may be higher than 1000°F but it was not investigated at that time for fear of carbon deposition. Later studies showed that G-65 has an upper temperature limit of 1200°F in the presence of steam, but the overall activity was not impressive.

• CCI C-13-4 fell between the Harshaw Ni-0104T and Girdler G-65.

• Engelhard 12468 has the best low-temperature activity as expected from a ruthenium catalyst, but was not impressive at higher temperatures. The economics and the susceptibility to be poisoned precluded performing extensive investigations.

5.5.4 Pore Diffusion

Pore-diffusion resistance will be encountered at higher temperatures, or higher carbon monoxide concentrations, and larger catalyst sizes. The effect of pore diffusion resistance on the measured reaction rates was investigated. Rates were measured at comparable temperatures and concentrations while particle size was varied. The results are presented in Tables 5-17 to 5-20. These runs indicated not only a first order dependence on carbon monoxide, but also some dependence on hydrogen and methane concentrations for the methanation reaction. Steam produced from the methanation reaction does not affect the rate, but it is not known if large quantities of steam will be added to the feed. Further evidence to support the diffusional influence was the virtual lack of carbon dioxide production found when small catalyst particles were used. With large pellets, a measurable amount of carbon dioxide was always produced, which is indicative of the carbon dioxide shift reaction occurring deep in the porous structure. With the small particles, the carbon monoxide and steam could be removed more easily from the surface without further reaction.

5.5.5 Effect of Low H_2/CO Ratio

The rate of methane formation slows when the hydrogen-to-carbon monoxide ratio in the feed is less than 3.15. It becomes poorer as the ratio decreases, and some catalysts showed permanent deactivation when the hydrogen-to-carbon monoxide ratio was less than 2.0. Carbon deposition usually is not a problem at temperatures less than 950°F and high hydrogen-to-carbon monoxide ratio, but becomes a problem at temperatures higher than 900°F and low H_2/CO ratios.

For most of the catalysts studied here at pressures of 600 psig or higher, it is recommended that a gas be fed at temperatures higher than 525°F and a hydrogen-to-carbon monoxide ratio greater than 20. It is also recommended that the methanation be performed at temperatures lower than 900°F for feed gases having a hydrogen-to-carbon monoxide ratio of less than 3.00. The attempts to regenerate those catalysts which were deactivated due to a low hydrogen-to-carbon monoxide ratio and undesirable temperatures were not successful. The data for the runs where hydrogen-to-carbon monoxide ratio was varied are presented in Tables 5-21 through 5-28.

Table 5-17. METHANATION DATA – EFFECT OF PARTICLE SIZE (Harshaw Ni-0104T, 18 mesh)

Run Number	126	127	128	129	130	131	132	133	134	135	136
Catalyst Weight, g	10.0	10.0	30.3	10.0	dust	5.0	5.0	5.0	5.0	5.0	5.0
Feed Gas Rate, SCF/hr	4.58	4.58	10.1	23.04	27.68	7.64	7.64	7.64	7.64	8.59	21.49
Feed Gas Composition, mole %											
Helium	2.69	2.69	2.69	2.69	2.69	2.69	2.69	1.0	1.0	1.0	1.0
Carbon Monoxide	10.7	10.7	10.7	10.7	10.7	10.7	10.7	10.9	10.9	10.9	10.9
Carbon Dioxide	3.01	3.01	3.01	3.01	3.01	3.01	3.01	3.1	3.1	3.1	3.1
Hydrogen	30.4	30.4	30.4	30.4	30.4	30.4	30.4	30.9	30.9	30.9	30.9
Methane	51.6	51.6	51.6	51.6	51.6	51.6	51.6	52.5	52.5	52.5	52.5
Ethane	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	548	550	650	650	650	650	650	650	650	650	650
Reactor Pressure, psig	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	2.87	2.89	9.65	16.2	27.30	6.81	6.86	6.95	7.26	7.26	19.60
Product Gas Composition, mole %											
Helium	4.5	4.0	6.1	3.9	5.0	5.7	5.3	1.2	1.2	1.1	1.0
Carbon Monoxide	0.3	0.4	3.0	3.7	9.8	4.2	5.0	5.2	6.6	6.9	9.0
Carbon Dioxide	6.8	6.9	5.9	4.2	3.4	4.7	4.6	4.7	4.4	3.5	3.7
Hydrogen	1.5	1.6	22.8	4.3	29.4	12.1	13.4	14.3	16.7	17.8	24.3
Methane	91.3	86.1	61.3	82.9	50.8	71.7	70.1	72.9	69.3	68.9	60.2
Ethane	1.1	1.0	0.9	1.0	1.6	1.6	1.6	1.7	1.8	1.8	1.8
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.83	2.83	2.83	2.83
Water Collected, lb/hr x 10^4	521	414	132	748	62	--	264	264	--	213	286
Rate of Methane Formation, lb-mol/hr-g catalyst x 10^4	0.67	0.32	0.68	4.00	--	2.75	2.46	2.44	1.84	2.26	3.00

Table 5-18. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156
Catalyst Weight, g	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8
Feed Gas Rate, SCF/hr	8.27	9.98	4.70	5.15	6.19	5.60	8.00	9.12	10.3	11.8	38.0	32.6	28.5	23.2	18.0	17.9	6.30	7.98	9.82	11.7
Feed Gas Composition, mole %																				
Nitrogen	0.0										0.0									
Helium	0.0										0.0									
Carbon Monoxide	10.0										6.6									
Carbon Dioxide	2.5	Same as Run 137									2.3	Same as Run 147								
Hydrogen	31.1										23.6									
Methane	56.1										67.0									
Ethane	0.2										0.4									
Propane	0.1										0.1									
Total	100.0										100.0									
Reactor Temperature, °F	550	550	750	750	550	525	525	550	550	550	550	550	650	650	550	950	950	700	550	550
Reactor Pressure, psig	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	6.25	7.47	3.27	3.86	4.62	4.11	6.03	6.95	8.05	9.27	34.2	28.9	25.9	21.1	15.3	15.5	5.16	6.47	8.10	9.77
Product Gas Composition, mole %																				
Nitrogen	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	3.0	4.9	1.1	1.4	2.2	1.7	2.7	3.0	3.9	3.9	4.5	4.5	3.9	3.6	3.6	3.4	0.5	1.9	2.3	0.9
Carbon Dioxide	3.1	2.9	3.7	3.51	3.2	3.3	3.0	3.0	2.8	2.8	2.1	2.1	2.1	2.1	2.1	2.1	2.3	2.2	2.1	2.2
Hydrogen	7.7	10.5	3.6	4.5	6.3	5.3	7.5	8.6	9.8	10.9	15.3	14.6	13.0	12.3	10.9	9.1	4.8	5.4	6.6	8.2
Methane	85.9	81.3	91.4	90.4	88.0	89.5	86.4	84.9	83.1	82.0	77.6	78.3	80.5	81.5	82.9	84.9	92.0	90.2	88.6	88.2
Ethane	0.3	0.4	0.2	0.2	0.3	0.2	0.3	0.4	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.4	0.5
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.11	3.58	3.58	3.58	3.58	3.58	3.58	3.58	3.58	3.58	3.58
Water Collected, lb/hr x 10^4	292	338	185	204	237	223	301	344	334	364	458	434	385	335	315	318	160	195	227	249
Rate of Methane Formation, lb/mol/hr-g catalyst x 10^4	1.60	1.04	0.77	1.32	1.30	1.18	1.59	1.72	2.00	2.16	2.37	1.73	3.86	3.64	1.37	2.57	1.16	1.08	1.31	1.71

Table 5-19. METHANATION DATA – CATALYST EVALUATION (Girdler G-65)*

Run Number	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175
Catalyst Weight, g	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9	21.9
Feed Gas Rate, SCF/hr	5.75	4.37	4.57	3.41	3.41	3.41	3.33	7.93	5.76	8.45	11.88	15.34	15.51	10.08	7.39	7.30	10.18	15.57	7.61
Feed Gas Composition, mole %																			
Nitrogen	1.7																		
Helium	1.0																		
Carbon Monoxide	10.7																		
Carbon Dioxide	3.0																		
Hydrogen	30.4	Same as Run 157																	
Methane	51.6																		
Ethane	1.6																		
Propane	0.0																		
Total	100.0																		
Reactor Temperature, °F	700	700	750	750	800	851	850	850	850	850	1050	1050	750	750	750	800	800	800	700
Reactor Pressure, psig	1000	1004	1000	1000	1000	1000	1000	1000	998	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Product Gas Rate, SCF/hr	5.23	3.84	3.99	2.69	2.67	2.64	2.61	6.58	4.42	7.06	10.25	14.47	14.19	8.78	6.68	6.40	9.02	14.14	6.72
Product Gas Composition, mole %																			
Nitrogen	2.5	2.1	2.2	2.4	2.3	2.2	2.2	2.0	2.2	2.0	2.0	1.7	2.2	2.0	1.9	1.8	2.0	1.8	2.0
Helium	1.1	1.2	1.1	1.6	1.3	1.3	1.3	1.1	1.3	1.1	1.1	1.0	1.9	1.5	1.1	1.2	1.1	1.1	1.1
Carbon Monoxide	10.8	9.3	7.2	5.9	8.3	5.2	5.3	8.9	8.1	9.3	10.6	10.8	10.8	11.5	10.5	10.6	10.4	10.9	11.7
Carbon Dioxide	5.0	5.3	5.4	5.3	5.4	5.4	5.2	4.8	4.9	4.7	4.5	4.3	4.4	4.6	4.8	5.0	4.6	4.6	4.5
Hydrogen	21.0	18.3	16.4	12.6	9.5	9.9	9.8	13.9	8.7	14.9	18.8	25.1	24.9	20.2	21.9	19.5	20.8	22.8	21.5
Methane	58.7	62.9	67.1	71.6	72.7	75.6	75.8	68.8	74.3	67.5	62.4	56.6	55.1	59.5	59.1	61.3	60.5	58.2	58.5
Ethane	0.9	0.9	0.6	0.6	0.5	0.4	0.4	0.5	0.5	0.5	0.6	0.5	0.7	0.7	0.7	0.6	0.6	0.6	0.7
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84	2.84
Water Collected, lb/hr x 10^4	172	207	178	229	192	241	135	390	333	409	402	555	377	367	279	321	370	437	141
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	0.06	0.14	0.34	0.18	0.18	0.28	0.26	0.31	0.31	0.34	0.22	0.09	0.15	0.05	0.10	0.12	0.21	0.15	0.03

*Feed gas contained 0.8 ppm ethyl mercaplan and 0.5 hydrogen sulfide.

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Table 5-20. METHANATION DATA - EFFECT OF PARTICLE SIZE
(Harshaw Ni-0101 Catalyst, -40 +60 mesh)

Run Number	176	177	178	179	180	181	182
Catalyst Weight, g	0.37	0.37	0.37	0.37	0.37	0.37	0.37
Feed Gas Rate, SCF/hr	4.43	4.25	4.69	4.59	4.45	4.56	4.51
Feed Gas Composition, mole %							
Nitrogen	--	--	--	--	--	--	--
Helium	70.85	75.50	79.75	85.68	74.67	77.48	78.52
Carbon Monoxide	5.25	5.10	5.15	5.22	5.03	2.92	1.78
Carbon Dioxide	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hydrogen	23.8	19.3	15.0	9.0	20.2	19.5	19.6
Methane	--	--	--	--	--	--	--
Ethane	--	--	--	--	--	--	--
Propane	--	--	--	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, ^{0}F	575	575	575	575	575	575	575
Reactor Pressure, psig	74	740	440	147	74	74	74
Product Gas Rate, SCF/hr	4.26	3.60	4.53	4.32	4.44	4.38	4.38
Product Gas Composition, mole %							
Nitrogen	--	--	--	--	--	--	--
Helium	75.96	80.19	83.35	87.74	78.01	80.39	81.32
Carbon Monoxide	3.62	4.18	4.18	4.65	4.43	1.97	0.83
Carbon Dioxide	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hydrogen	18.9	14.6	11.6	7.0	16.8	16.8	16.9
Methane	1.42	0.93	0.77	0.51	0.66	0.74	0.85
Ethane	--	--	--	--	--	--	--
Propane	--	--	--	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO Ratio	4.53	3.78	2.91	1.72	3.87	6.68	11.0
Water Collected, lb/hr x 10^{4}	28.2	15.6	16.3	10.3	13.7	15.2	17.4
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^{4}	4.19	2.31	2.41	1.52	2.03	2.26	2.42

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Table 5-21. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	183	184	185	186	187	188	189	190	191	192	193
Catalyst Weight, g	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6	8.6
Feed Gas Rate, SCF/hr	19.50	18.39	11.99	5.84	6.17	18.15	18.74	11.57	5.21	5.19	9.22
Feed Gas Composition, mole %											
Nitrogen	3.34										
Helium	0.0										
Carbon Monoxide	4.04										
Carbon Dioxide	0.48										
Hydrogen	19.90										
Methane	68.24										
Ethane	4.00										
Propane	0.0										
Total	100.00										
Reactor Temperature, °F	550	550	550	550	650	650	750	750	750	850	850
Reactor Pressure, psig	998	1000	1000	1000	998	1000	998	1002	1000	1000	1000
Product Gas Rate, SCF/hr	18.23	16.89	10.95	5.15	4.88	16.39	16.85	10.32	4.66	4.34	8.33
Product GasComposition, mole %											
Nitrogen	3.48	3.70	3.75	3.90	4.03	3.85	3.78	3.86	3.91	3.75	3.48
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	2.03	1.95	1.39	0.68	0.37	0.95	0.84	0.55	0.39	0.44	0.57
Carbon Dioxide	0.47	0.46	0.40	0.40	0.57	0.60	0.73	0.71	0.65	0.58	0.65
Hydrogen	13.09	12.85	12.20	9.72	2.17	4.55	6.80	3.13	2.17	3.95	4.25
Methane	76.83	76.85	78.50	81.85	91.65	87.59	86.37	90.70	92.30	90.89	90.36
Ethane	4.10	4.19	3.76	3.45	1.21	2.46	1.48	1.05	0.58	0.39	0.69
Propane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO Ratio	4.92	4.92	4.92	4.92	4.92	4.92	4.92	4.92	4.92	4.92	4.92
Water Collected, lb/hr x 10^4	211	151	143	86	308	235	203	203	74	46	95
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	1.27	1.24	1.00	0.61	0.69	1.74	1.85	1.23	0.58	0.58	0.98

Same as Run 183

Table 5-22. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	194	195	196	197	198	199	200	201	202
Catalyst Weight, g	2.04	2.04	2.04	2.04	2.04	2.04	2.04	2.04	2.04
Feed Gas Rate, SCF/hr	7.80	5.47	7.84	4.06	4.00	3.94	4.10	3.55	4.34
Feed Gas Composition, mole %									
Nitrogen	--	--	--	--	--	--	--	--	--
Helium	18.3	36.5	55.1	69.5	61.2	22.8	22.8	83.2	55.1
Carbon Monoxide	8.4	8.6	8.1	7.3	8.2	8.6	8.6	4.9	8.1
Carbon Dioxide	--	--	--	--	--	--	--	--	--
Hydrogen	73.3	54.9	36.8	23.2	30.6	68.6	68.6	11.9	36.8
Methane	--	--	--	--	--	--	--	--	--
Ethane	--	--	--	--	--	--	--	--	--
Propane	--	--	--	--	--	--	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	575	575	775	975	875	575	575	575	575
Reactor Pressure, psig	573	573	573	280	278	578	280	281	281
Product Gas Rate, SCF/hr	5.49	4.31	6.59	3.54	3.62	3.54	3.58	3.47	3.89
Product Gas Composition, mole %									
Nitrogen	--	--	--	--	--	--	--	--	--
Helium	26.0	46.4	65.8	79.6	72.9	26.2	26.0	85.2	61.6
Carbon Monoxide	3.7	3.9	3.6	3.7	3.8	3.8	3.9	3.9	4.1
Carbon Dioxide	--	--	--	--	--	--	--	--	--
Hydrogen	62.2	42.9	24.6	12.1	18.1	64.2	65.1	9.7	29.4
Methane	8.1	6.8	6.0	4.6	5.2	5.8	5.0	1.2	4.9
Ethane	--	--	--	--	--	--	--	--	--
Propane	--	--	--	--	--	--	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	8.7	6.4	4.5	3.2	3.7	8.0	8.0	2.4	4.5
Water Collected, lb/hr x 10^4	449	896	164	73	92	96	114	19	111
Rate of Methane Formation, lb-mole/hr-g catalyst x 10^4	5.66	3.73	5.03	2.07	2.55	2.77	2.28	0.52	2.42

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Table 5-23. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	203	204	205	206	207	208	209	210	211	212	213	214
Catalyst Weight, g	2.04	2.04	2.07	2.07	2.07	2.07	2.07	2.07	2.03	2.03	2.03	2.03
Feed Gas Rate, SCF/hr	3.775	3.577	3.895	3.718	3.686	3.744	3.690	3.828	3.715	5.260	3.843	3.885
Feed Gas Composition, mole %												
Helium	56.97	67.4	63.18	61.71	68.20	77.34	77.93	51.9	37.10	50.20	42.90	0.05
Hydrogen	32.10	21.7	25.60	26.75	20.50	11.90	11.05	36.5	52.60	41.80	47.60	89.70
Carbon Monoxide	10.93	10.9	11.10	11.45	11.22	10.65	10.90	11.5	10.30	7.90	9.40	10.20
Carbon Dioxide	--	--	0.12	0.09	0.08	0.11	0.12	0.1	0.03	0.04	0.03	0.05
Methane	--	--	--	--	--	--	--	--	--	--	--	--
Total	100.00	100.0	100.00	100.00	100.00	100.00	100.00	100.0	100.03	99.94	99.93	100.00
Reactor Temperature, °F	573	575	573	575	574	573	576	578	572	573	448	577
Reactor Pressure, psig	298	300	600	602	598	607	602	601	599	573	600	598
Product Gas Rate, SCF/hr	3.731	--	3.214	3.238	3.417	3.343	3.660	3.284	2.711	4.466	3.799	3.019
Product GasComposition												
Helium	57.63	--	70.04	70.55	74.98	85.32	78.76	60.47	49.40	59.70	43.33	--
Hydrogen	31.20	--	16.30	15.62	12.83	8.15	10.35	26.17	36.40	31.00	47.16	86.88
Carbon Monoxide	10.75	--	7.35	7.05	8.10	3.85	10.37	9.30	4.00	3.50	9.29	6.20
Carbon Dioxide	0.12	--	1.06	0.82	0.84	0.76	0.17	0.31	0.34	0.19	0.10	0.12
Methane	0.30	--	5.25	5.96	3.25	1.92	0.35	3.75	9.90	5.60	0.12	6.80
Total	100.00	--	100.00	100.00	100.00	100.00	100.00	100.00	100.04	99.99	100.00	100.00
Feed H_2/CO Ratio	2.94	--	2.31	2.34	1.83	1.12	1.01	3.17	5.11	5.29	5.06	8.79
Water Collected, lb/hr x 10^4	--	--	137.5	--	57.3	--	--	22.0	167.6	132.3	--	88.2
Rate of Methane Formation lb-mole/hr-g catalyst x 10^4	0.34	--	2.12	2.42	1.40	0.82	0.15	1.54	3.40	3.50	0.05	2.62

Table 5-24. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	215	216	217	218	219	220	221	222	223	224	225	226
Catalyst Weight, g	2.03	2.0521	2.0521	2.0521	2.0521	2.0521	2.0521	2.0361	2.0216	2.0216	2.0216	2.0216
Feed Gas Rate, SCF/hr	5.396	5.290	3.596	3.747	6.541	3.494	4.169	3.455	7.495	4.135	3.725	7.634
Feed Gas Composition, mole %												
Helium	53.20	55.81	2.06	26.70	32.00	13.70	12.84	59.52	56.27	53.83	57.25	55.72
Hydrogen	40.70	33.50	88.40	61.60	57.40	75.40	76.70	28.00	31.00	33.00	30.00	31.50
Carbon Monoxide	6.10	10.60	9.50	9.90	9.90	9.20	9.00	11.67	11.35	11.72	11.35	12.00
Carbon Dioxide	0.02	0.09	0.04	0.04	0.04	0.04	0.06	0.05	0.08	0.10	0.10	0.08
Methane	--	--	--	1.70	0.69	1.60	1.40	0.76	1.30	1.35	1.30	0.7
Total	100.02	100.00	100.00	99.94	100.03	99.94	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, °F	573	575	576	576	576	500	575	576	576	523	574	573
Reactor Pressure, psig	603	573	600	600	600	600	600	301	299	299	299	300
Product Gas Rate, SCF/hr	4.881	4.719	2.792	2.896	5.433	3.082	2.994	2.868	6.452	3.568	3.013	6.010
Product GasComposition												
Helium	58.80	63.50	2.66	34.1	38.20	15.70	17.4	71.48	65.56	62.91	69.83	61.46
Hydrogen	34.70	24.73	85.11	52.2	50.40	73.30	67.3	12.65	19.60	21.90	15.10	22.25
Carbon Monoxide	3.90	4.19	3.98	3.8	5.60	7.00	4.6	4.54	6.20	7.63	4.35	7.58
Carbon Dioxide	0.08	0.49	0.24	0.2	0.19	0.10	0.2	1.25	0.74	0.31	0.72	0.66
Methane	2.50	7.09	8.01	9.6	5.61	3.89	10.5	10.08	7.90	7.25	10.00	8.05
Total	99.98	100.00	100.00	99.9	99.99	99.99	100.0	100.00	100.00	100.00	100.00	100.00
Feed H_2CO Ratio	6.67	3.16	9.31	6.22	5.80	8.19	8.52	2.40	2.73	2.82	2.64	2.63
Water Collected, lb/hr x 10^4	57.8	158.70	26.46	22.04	211.64	--	123.46	22.0	132.28	22.0	22.1	116.84
Rate of Methane Formation lb-mole/hr-g catalyst x 10^4	1.58	4.23	2.83	3.52	3.86	0.81	3.97	3.39	5.30	2.88	3.25	5.53

Table 5-25. METHANATION DATA – CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	227	228	229	230	231	232	233	234	235	236
Catalyst Weight, g	2.0113	2.0113	2.0113	2.0113	2.0113	2.0113	2.0113	2.0113	2.0113	2.0113
Feed Gas Rate, SCF/hr	3.567	4.266	3.608	4.367	4.239	3.891	4.056	3.803	3.886	3.871
Feed Gas Composition, mole %										
Helium	--	--	--	--	--	--	--	--	--	--
Hydrogen	28.0	17.5	22.7	38.4	28.8	11.9	15.3	14.1	27.2	32.8
Carbon Monoxide	10.1	9.9	9.5	9.2	9.5	10.4	4.6	4.73	9.75	9.73
Carbon Dioxide	0.1	0.16	0.03	0.14	0.15	0.16	0.15	0.13	0.18	0.15
Methane	61.8	72.44	67.77	52.26	61.55	77.54	79.95	81.04	52.87	57.32
Total	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, ^{0}F	575	575	573	573	577	575	576	575	525	575
Reactor Pressure, psig	600	600	601	299	299	300	301	300	298	298
Product Gas Rate, SCF/hr	3.066	3.523	3.169	3.936	3.862	3.690	3.886	3.651	3.624	3.452
Product Gas Composition										
Helium	--	--	--	--	--	--	--	--	--	--
Hydrogen	15.5	4.7	10.7	30.0	21.2	5.1	11.5	9.9	22.9	24.6
Carbon Monoxide	5.45	6.48	6.41	6.58	7.11	8.09	3.12	3.18	8.16	7.13
Carbon Dioxide	0.84	0.96	0.39	0.42	0.42	0.70	0.58	0.33	0.23	0.32
Methane	78.21	87.86	82.5	63.0	71.27	86.11	84.8	86.59	68.71	67.95
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO Ratio	2.76	1.76	2.38	4.12	3.01	1.15	3.31	2.98	2.78	3.37
Water Collected, lb/hr x 10^4	33.07	22.05	--	35.27	28.66	39.68	--	17.64	26.46	--
Rate of Methane Formation, lb-mole/hr-g catalyst x 10^4	2.21	2.06	1.74	1.89	1.37	1.29	0.66	0.70	0.98	1.52

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Table 5-26. METHANATION DATA - CATALYST EVALUATION (Harshaw Ni-0104T)

Run Number	237	238	239	240	241	242	243	244	245
Catalyst Weight, g	2.0878	2.0878	2.0878	2.0878	2.0878	2.0878	2.0878	1.9107	1.9107
Feed Gas Rate, SCF/hr	3.710	3.987	3.778	4.082	3.652	3.870	3.637	3.898	3.610
Feed Gas Composition, mole %									
Helium	--	--	--	--	--	--	--	--	--
Hydrogen	30.8	11.0	16.9	29.0	10.7	12.99	25.8	25.51	34.1
Carbon Monoxide	8.9	9.2	10.3	10.4	4.8	5.1	9.2	9.95	9.5
Carbon Dioxide	0.13	0.18	0.18	0.27	0.42	--	0.28	0.54	0.52
Methane	60.17	79.62	72.62	60.33	84.08	81.91	64.72	64.0	55.88
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, ^{0}F	575	575	575	576	575	576	525	576	575
Reactor Pressure, psig	601	600	598	601	601	603	601	577	596
Product GasRate, SCF/hr	3.177	3.603	3.454	3.672	3.447	3.679	3.288	3.389	3.059
Product Gas Composition									
Helium	--	--	--	--	--	--	--	--	--
Hydrogen	17.8	2.8	9.5	22.6	2.0	8.4	17.5	16.67	24.9
Carbon Monoxide	6.2	7.2	8.4	8.1	3.8	3.6	7.5	5.57	5.1
Carbon Dioxide	0.56	0.76	0.60	0.50	0.44	0.4	0.31	0.93	0.83
Methane	75.44	89.24	81.5	68.8	93.76	87.6	74.69	76.83	69.17
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Feed H_2/CO									
Feed H_2/CO Ratio	3.43	1.19	1.64	2.78	2.20	2.25	2.80	2.56	3.58
Water Collected, lb/hr x 10^4	11.02	15.43	13.23	30.86	6.61	--	--	190.7	52.9
Rate of Methane Formation, lb-mole/hr-g catalyst x 10^4	2.28	1.08	1.03	1.41	2.00	0.65	1.27	1.48	1.34

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Table 5-27. METHANATION DATA - CARBON DEPOSITION AND LOW TEMPERATURE STUDY (Harshaw Ni-0104T)

Run Number	246	247	248	249	250*
Catalyst Weight, g	1.91	1.91	1.91	1.91	2.09
Feed Gas Rate, SCF/hr	3.92	4.40	4.02	4.02	2.38
Feed Gas Composition, mole %					
Nitrogen	0.26	0.0	0.0	0.24	0.0
Helium	0.0	0.0	0.0	0.0	
Carbon Monoxide	0.0	99.4	0.14	0.0	10.2
Carbon Dioxide	0.67	0.4	0.03	0.67	2.1
Hydrogen	0.0	0.0	99.78	0.0	27.5
Methane	96.2	0.2	0.05	96.3	10.4
Ethane	2.4	0.0	0.0	2.4	0.0
Propane	0.47	0.0	0.0	0.39	0.0
Total	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, ^{0}F	575	575	575	575	400
Reactor Pressure, psig	597	600	604	602	597
Product Gas Rate, SCF/hr	3.92	4.40	3.99	3.97	--
Product Gas Composition, mole %					
Nitrogen	0.26	0.0	0.0	0.26	--
Helium	0.0	0.0	0.0	0.0	--
Carbon Monoxide	0.0	99.4	0.06	0.0	--
Carbon Dioxide	0.67	0.4	0.04	0.67	--
Hydrogen	0.0	0.0	99.77	0.0	--
Methane	96.2	0.2	0.13	96.3	--
Ethane	2.4	0.0	0.0	2.4	--
Propane	0.47	0.0	0.0	0.37	--
Total	100.00	100.00	100.00	100.00	--
Feed H_2/CO Ratio	--	--	--	--	--
Water Collected, lb/hr x 10^4	0	0	0	0	--
Rate of CO Conversion, lb mole/hr-g catalyst x 10^4	--	--	--	--	--

*Nickel was stripped from the catalyst and deposited on the bottom of the reactor.

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Table 5-28. METHANATION DATA – EFFECT OF H_2/CO RATIO ON METHANATION RATE

Run Number	251	252	253	254	255	256	257
Catalyst Weight, g	2.12	2.12	2.12	2.12	2.12	2.12	2.12
Feed Gas Rate, SCF/hr	3.74	4.10	3.64	3.71	3.78	3.67	3.84
Feed Gas Composition, mole %							
Nitrogen	1.2	0.6	--	--	1.4	0.4	0.3
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	9.9	9.0	11.8	10.1	8.8	10.3	9.9
Carbon Dioxide	0.4	0.3	0.3	0.1	0.2	0.2	0.2
Hydrogen	31.1	41.7	41.0	48.0	24.1	27.5	30.2
Methane	55.8	47.0	45.6	41.4	64.5	60.7	58.4
Ethane	1.4	1.2	1.1	0.3	0.8	0.8	0.8
Propane	0.2	0.2	0.2	0.1	0.2	0.1	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	575	575	576	575	575	576	576
Reactor Pressure, psig	595	598	598	600	600	301	604
Product Gas Rate, SCF/hr	3.05	3.27	3.21	3.13	3.21	3.55	3.44
Product Gas Composition, mole %							
Nitrogen	0.7	0.8	--	--	1.4	0.5	0.5
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Carbon Monoxide	6.5	5.0	7.1	6.5	6.0	7.4	6.8
Carbon Dioxide	0.8	0.4	0.5	0.2	0.4	0.4	0.3
Hydrogen	16.5	27.3	30.9	39.9	12.0	19.9	24.1
Methane	73.7	65.0	60.0	52.7	79.2	70.8	67.4
Ethane	1.5	1.3	1.3	0.5	0.8	0.8	0.8
Propane	0.3	0.2	0.2	0.2	0.2	0.2	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	3.14	4.63	3.47	4.75	2.74	2.67	3.05
Water Collected, lb/hr x 10^4	44	--	--	66	48	116	26
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	1.60	2.48	2.56	2.02	1.62	1.52	1.76

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5.5.6 Effect of Excess Methane in the Feed to the Methanator

The presence of large amounts of methane in the feed has some effect on the rate of methanation. The effect becomes greater when the relative partial pressure of methane is much higher than that of hydrogen. In general, excess methane in feed gas tends to decrease the rate of methane formation and the reaction order appears to be between 0 and –1 for HYGAS conditions. The reaction order may be more negative for low-pressure coal gasification processes.

The effect of excess methane in feed on the rate of formation of methane is shown in Figures 5-15 and 5-16.

5.5.7 Effect of Benzene in the Feed to the Methanator

The presence of 1 mole percent (water-free basis) benzene or less has no effect on the methanation catalysts. The benzene in feed comes through as benzene, cyclohexane and lighter hydrocarbons. The presence of more than 1 mole percent benzene tends to decrease the methanation activity gradually and step-wise. For example, the catalyst activity will drop gradually about 10 percent and will remain there for a long time, then it will gradually drop another 10 percent and hold there for a while, and so on. The temperature of the methanator must not run away while benzene is present, because carbon will be deposited. Excess carbon was found in the catalyst when it was deactivated by benzene. Most of the catalyst studied here were not regenerable after benzene deactivation. The results of these studies are presented in Tables 5-29 to 5-34.

It is difficult to obtain an accurate material balance on benzene because of the inaccuracy in both quantitative and qualitative analyses of liquid samples. Due to the long transfering lines and dead spaces in the system, the amount of liquid collected at the end of each run may not be the amount produced by the current run. In addition, the quantity collected was too small for a good qualitative analysis. Nevertheless, an increase in the methane content in the product was noticed and occasionally, the presence of cyclohexane was detected in the vapor phase. Carbon was deposited on both G-65 (Run 264) and Harshaw Ni-0104T (Run 275) catalysts when temperature was increased. The upper temperature limits of the catalysts must be lowered when benzene or other aromatics are present in the feed gas.

5.5.8 Effect of CO_2 on the Methanation Catalyst

This study was concerned with possible poisoning effects that carbon dioxide might have on the methanation catalysts. If the presence of carbon dioxide in the methanator does not affect the rate of methanation or the catalyst, carbon dioxide may be used to consume the excess hydrogen and thus increase the heating value of the final product. Another objective of this study was also designed to determine the conditions at which carbon dioxide can be hydrogenated to methane. Data for this study are presented at several places in this part of the HYGAS Final Report but some of the more concentrated studies are presented in Tables 5-35 to 5-38.

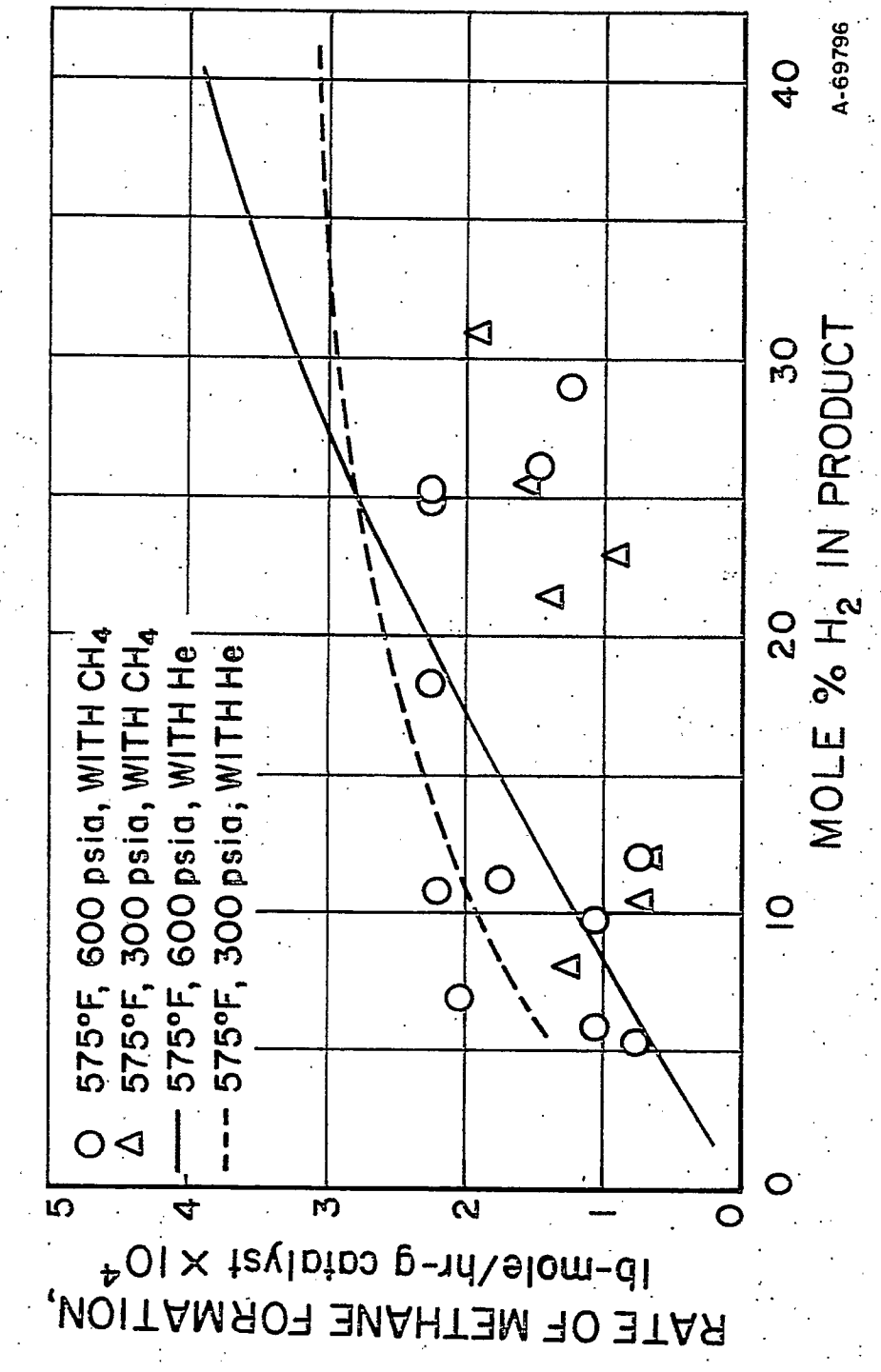

Figure 5-15. THE EFFECT OF EXCESS METHANE IN THE FEED ON THE RATE OF FORMATION OF METHANE AT DIFFERENT PRESSURES

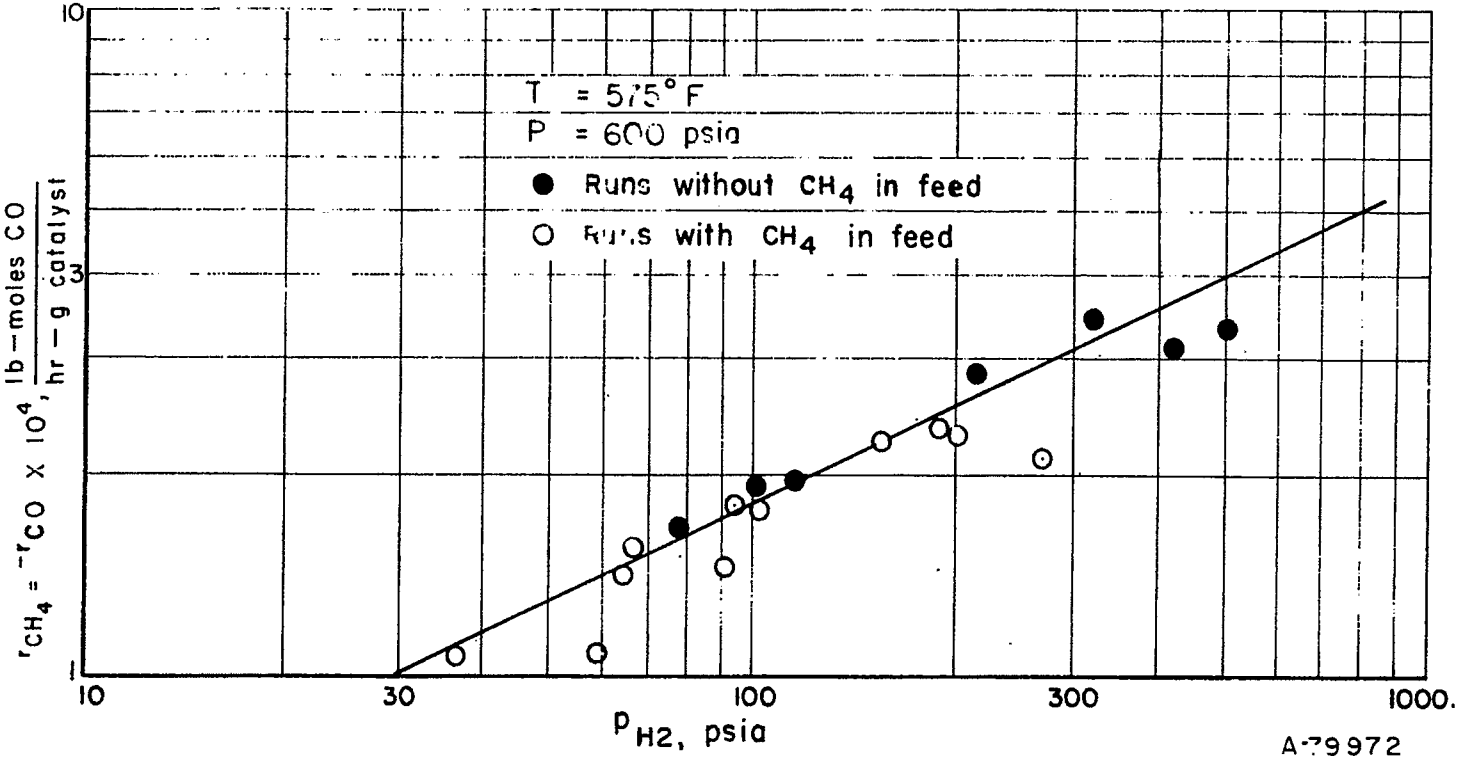

Figure 5-16. THE EFFECT OF METHANE IN THE FEED ON THE RATE OF CONVERSION OF CO AT VARIOUS HYDROGEN PARTIAL PRESSURES

Table 5-29. METHANATION DATA – EFFECT OF BENZENE ON THE ACTIVITY OF METHANATION CATALYSTS

Run Number	258	259	260	261a	261b	261c	262a	262b	262c	263a	263b	263c	264a	264b
Catalyst Weight, g	2.02	2.02	2.02	2.08	2.08	2.08	2.14	2.14	2.14	2.14	2.14	2.14	2.14	2.14
Feed Gas Rate, SCF/hr	4.04	3.77	3.63	3.74	3.74	3.74	3.71	3.71	3.71	3.76	3.76	3.76	3.79	3.79
Feed Gas Composition, mole %														
Nitrogen	0.6	0.4	0.4	0.2			0.2			0.1			0.1	
Helium	0.0	0.0	0.0	0.0			0.0			0.0			0.0	
Carbon Monoxide	10.0	10.2	5.5	8.5			9.0			9.2			9.0	
Carbon Dioxide	0.2	0.2	0.2	0.2			0.2			0.2			0.2	
Hydrogen	36.6	40.5	20.9	30.0			24.8			31.2			32.5	
Methane	51.8	48.0	70.9	59.6			63.8			57.2			56.6	
Ethane	0.7	0.6	0.9	0.5			0.7			0.5			0.5	
Propane	0.1	0.1	0.2	--			0.1			0.1			0.1	
Benzene	0.0	0.0	1.0	1.0			1.2			1.5			1.0	
Total	100.0	100.0	100.0	100.0			100.0			100.0			100.0	
Reactor Temperature °F	575	576	577	575	576	574	576	576	576	576	576	576	950	950
Reactor Pressure, psig	600	602	603	305	300	301	298	298	298	297	297	297	298	299
Product Gas Rate, SCF/hr	3.31	3.07	3.37	3.43	3.70	3.52	3.58	3.58	3.58	2.90	2.89	2.90	2.93	1.35
Product Gas Composition, mole %														
Nitrogen	0.5	0.6	0.6	0.3	0.3	0.3	0.2	0.2	0.2	0.1	0.1	0.1	0.1	--
Helium	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	--
Carbon Monoxide	5.7	5.3	3.2	6.0	7.0	7.7	5.0	6.1	5.4	5.8	6.8	6.1	5.8	--
Carbon Dioxide	0.5	0.5	0.3	0.4	0.4	0.4	0.5	0.5	0.5	0.5	0.6	0.5	0.5	--
Hydrogen	23.2	27.4	16.5	22.5	25.1	24.8	18.0	19.0	18.8	10.1	10.1	10.4	22.0	--
Methane	69.2	65.4	77.6	70.1	66.4	66.0	75.5	73.3	74.2	82.3	81.1	81.7	70.7	--
Ethane	0.7	0.7	0.9	0.7	0.7	0.7	0.7	0.7	0.7	1.0	1.1	1.0	0.7	--
Propane	0.2	0.1	0.2	--	0.07	0.07	0.1	0.13	0.13	0.12	0.12	0.12	0.1	--
Benzene	0.0	0.0	0.7	0.0	0.03	0.03	--	0.07	0.07	0.08	0.08	0.08	0.1	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	--
Feed H_2/CO Ratio	3.66	3.97	3.80	3.53	3.53	3.53	2.76	2.76	2.76	3.39	3.39	3.39	3.61	--
Water Collected, lb/hr x 10^4	176	66	35	--	--	--	22	26	24	46	57	84	39	--
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	2.54	2.72	1.14	1.40	0.74	0.58	1.88	1.40	1.70	2.16	1.81	2.05	2.78	--

Table 5-30. METHANATION DATA – EFFECT OF BENZENE ON THE ACTIVITY OF METHANATION CATALYSTS

Run Number	265	266	267	268	269	270	271	272	273	274	275	276
Catalyst Weight, g	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07	2.07
Feed Gas Rate, SCF/hr	3.83	3.62	3.81	3.60	3.95	3.57	3.97	3.73	3.75	4.00	3.21	3.21
Feed Gas Composition, mole %												
Nitrogen	--	--	--	--	--	--	--	--	--	--	--	--
Helium	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	6.8	6.7	6.0	7.4	2.1	9.2	3.8	9.3	0.8	13.9	5.9	0.8
Carbon Dioxide	0.1	0.1	0.1	0.1	0.04	0.03	0.04	0.04	0.04	0.08	0.07	0.9
Hydrogen	92.6	92.2	92.7	91.5	96.16	90.67	95.36	90.56	98.56	85.02	93.73	98.1
Methane	--	--	--	--	--	--	--	--	--	--	--	--
Ethane	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	0.5	1.0	1.2	1.0	1.7	0.1	0.8	0.1	0.6	1.0	0.3	0.2
Total	100.0	100.0	100.0	100.0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.0
Reactor Temperature, °F	575	575	573	575	575	574	573	575	574	575	875	875
Reactor Pressure, psig	595	598	596	598	593	597	592	598	597	591	594	596
Product Gas Rate, SCF/hr	3.31	2.95	3.27	3.14	3.68	3.03	3.63	3.07	3.74	2.88	2.88	3.10
Product Gas Composition, mole %												
Nitrogen	--	--	--	--	--	--	--	--	--	--	--	--
Helium	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	2.0	2.0	1.7	2.5	0.6	3.9	1.2	4.2	0.1	8.1	2.3	0.8
Carbon Dioxide	0.06	0.1	0.1	0.1	0.04	1.6	0.05	0.16	0.04	0.46	0.1	0.1
Hydrogen	89.44	89.6	90.3	88.9	94.96	87.1	93.35	88.14	98.36	77.54	92.4	98.6
Methane	8.5	8.3	7.9	8.5	4.4	7.4	5.4	7.5	1.5	13.9	5.2	0.5
Ethane	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--	--	--
Total	100.00	100.0	100.0	100.0	100.0	100.0	100.00	100.00	100.00	100.00	100.0	100.0
Feed H_2/CO Ratio	13.7	13.9	15.6	12.5	46.6	9.86	25.3	9.75	12.3	6.19	15.9	12.2
Water Collected, lb/hr x 10^4	--	22	13	15	--	4	46	9	--	84	31	39
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	2.43	2.41	2.26	2.76	0.97	2.04	1.56	2.95	0.28	3.67	1.71	0.03

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Table 5-31. METHANATION DATA – EFFECT OF BENZENE ON THE ACTIVITY OF METHANATION CATALYSTS

Run Number	277a	277b	277c	277d	277e	277f	277g	277h**	277i**	278a**	278b**	279a**	279b**
Catalyst Weight, g	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.10	2.15	2.15	2.02	2.02
Feed Gas Rate, SCF/hr	3.88	3.88	3.88	3.88	3.27	3.27	3.27	3.27	3.27	4.09	4.09	3.78	3.78
Feed Gas Composition, mole %													
Nitrogen	--	--	--	--	--	--	--	--	--	1.5	1.5	0.6	0.6
Helium	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	8.1	8.6	8.1	8.1	8.0	8.0	8.0	8.0	8.0	8.3	8.3	8.2	8.0
Carbon Dioxide	0.02	0.02	0.02	0.02	0.12	0.12	0.12	0.12	0.12	0.1	0.1	0.1	0.1
Hydrogen	27.6	27.6	27.6	27.6	27.9	27.9	27.9	27.9	27.9	26.0	26.0	27.2	26.5
Methane	64.18	63.18	64.18	63.38	63.88	62.88	63.88	62.38	63.88	61.5	64.0	63.8	62.2
Ethane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Propane	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	0.0	0.5	0.0	0.8	0.0	1.0	0.0	1.5	--	2.5	0.0	0.0	2.5
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, °F	573	574	575	575	575	577	576	576	576	575	574	578	578
Reactor Pressure, psig	597	595	595	596	597	595	596	596	596	300	300	298	299
Product Gas Rate, SCF/hr	3.57	3.81	3.73	3.58	2.83	2.80	2.96	2.85	2.89	3.53	3.35	3.28	3.30
Product Gas Composition, mole %													
Nitrogen	--	--	--	--	--	--	--	--	--	1.2	1.2	0.8	0.9
Helium	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	5.9	6.2	6.1	6.2	5.3	6.2	5.6	6.4	5.8	4.9	4.3	4.0	4.5
Carbon Dioxide	0.4	0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.3	0.4	0.6	0.5	0.5
Hydrogen	20.8	22.2	20.8	21.1	18.4	16.8	19.5	18.0	19.3	17.2	15.3	21.8	15.5
Methane	72.8	71.2	72.7	72.3	75.8	76.5	74.4	73.8	74.5	75.1	78.5	72.8	77.9
Ethane	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Propane	--	--	--	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	0.8	--	1.2	--	1.1	--	--	0.6
Total	100.0	100.0	100.0	100.0	100.0	99.9	100.0	99.8	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	3.41	3.21	3.41	3.41	3.48	3.48	3.48	3.48	3.48	3.13	3.13	3.13	3.31
Water Collected, lb/hr x 10^4	4	--	71	--	--	49	22	27	12	16	66	22	--
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	1.12	1.12	1.10	1.06	1.40	1.27	1.15	1.17	1.19	1.79	2.23	2.83	2.23

* Product gas contains 0.1 mole % cyclohexane.
** Product gas contains 0.2 mole % cyclohexane.

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Table 5-32. METHANATION DATA – RUN 280, EFFECT OF BENZENE ON THE METHANATION CATALYST (Harshaw Ni-0104T)

Time, hr.	4	13	23	28	51	82	102	116	122	135
Catalyst Weight, g	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11	2.11
Feed Gas Rate, SCF/hr	3.66	3.48	3.48	3.48	3.50	3.52	3.48	3.48	3.48	3.48
Feed Gas Composition, mole %										
Nitrogen	--	--	--	--	--	--	--	--	--	--
Helium	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
Carbon Dioxide	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hydrogen	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7	89.7
Methane	--	--	--	--	--	--	--	--	--	--
Ethane	--	--	--	--	--	--	--	--	--	--
Benzene	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	575	575	575	575	575	575	575	575	575	575
Reactor Pressure, psig	598	598	598	598	598	598	598	598	598	598
Product Gas Rate, SCF/hr	2.42	2.53	2.66	2.59	2.48	2.30	2.65	2.65	2.46	2.41
Product Gas Composition, mole %										
Nitrogen	--	--	--	--	--	--	--	--	--	--
Helium	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	2.7	2.9	3.1	3.0	3.3	3.5	3.8	4.2	4.2	4.2
Carbon Dioxide	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.3	0.3
Hydrogen	85.9	87.2	87.8	87.6	86.9	85.9	87.8	87.8	86.9	86.6
Methane	11.2	9.7	8.9	9.2	9.6	10.4	8.1	7.8	8.6	8.9
Ethane	--	--	--	--	--	--	--	--	--	--
Benzene	--	--	--	--	--	--	--	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75	9.75
Water Collected, lb/hr X 10^4	--	--	--	--	--	--	--	--	--	--
Rate of CO Conversion, lb-mol/hr-g catalyst X 10^4	3.35	3.02	2.92	2.94	2.94	2.95	2.65	2.54	2.61	2.64

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Table 5-33. METHANATION DATA – RUN 281, EFFECT OF BENZENE ON METHANATION CATALYST

Time, Hr	20	51	67	76	94	98
Catalyst Weight, g	2.08	2.08	2.08	2.08	2.08	2.08
Feed Gas Rate, SCF/hr	3.69	3.69	3.69	3.69	3.69	3.69
Feed Gas Composition, mole %						
Nitrogen	--					
Helium	--					
Carbon Monoxide	9.1					
Carbon Dioxide	0.3					
Hydrogen	28.3					
Methane	60.6					
Ethane	--					
Benzene	1.7					
Total	100.0					
Reactor Temperature, °F	574	574	574	574	574	574
Reactor Pressure, psig	301	301	301	301	301	301
Product Gas Rate, SCF/hr	2.96	3.05	2.80	2.84	2.85	2.94
Product Gas Composition, mole %						
Nitrogen	--	--	--	--	--	--
Helium	--	--	--	--	--	--
Carbon Monoxide	5.6	5.1	5.1	5.2	5.0	5.0
Carbon Dioxide	1.1	0.6	0.6	0.5	0.7	0.5
Hydrogen	12.8	14.8	7.3	11.4	12.0	12.5
Methane	80.5	79.5	87.0	82.9	82.3	82.0
Ethane	--	--	--	--	--	--
Benzene		--	--	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO ratio	3.11	3.11	3.11	3.11	3.11	3.11
Water Collected, lb/hr X 10^4	--	--	--	--	--	87
Rate of CO Conversion, lbmol/hr-g cat. X 10^4	1.66	1.97	2.11	2.05	2.11	2.06

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Table 5-34. METHANATION DATA – EFFECT OF BENZENE, MERCAPTANS, AND THIOPHENE (0.3 ppm propyl mercaptan and 0.8 ppm thiophene) ON METHANATION CATALYSTS

Run Number	282	283a	283b	283c	284	285	286	287	288	289	290	291	292	293	294	295	296	297
Catalyst Weight, g	2.07	2.10	2.10	2.10	2.09	2.09	2.09	2.09	2.09	2.09	2.09	2.04	2.04	2.04	2.04	2.04	2.08	2.12
Feed Gas Rate, SCF/hr	1.75	1.92	1.92	1.92	1.13	1.14	3.75	3.77	3.83	3.68	3.28	1.86	3.68	1.80	0.95	0.97	1.69	1.23
Feed Gas Composition, mole %																		
Nitrogen	--	--	--	--	--	0.7	--	0.7	0.2	0.3	0.1	--	--	--	--	0.2	--	0.5
Helium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	8.9	4.7	4.3	4.3	4.7	4.2	4.8	4.4	4.7	9.0	9.0	9.6	8.9	9.0	9.0	9.1	9.5	9.2
Carbon Dioxide	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Hydrogen	34.4	13.5	19.6	19.6	22.5	20.3	14.6	14.3	15.9	18.5	18.5	19.0	20.8	19.4	18.4	18.6	43.0	29.0
Methane	56.5	81.6	72.9	72.9	72.6	73.6	80.5	79.5	78.0	71.0	72.0	71.1	70.0	71.5	72.5	72.0	46.8	61.1
Ethane*	--	0.1	0.1	0.1	--	0.1	--	0.1	0.1	0.1	0.1	--	--	--	--	--	--	0.1
Benzene	--	--	3.0	3.0	--	1.0	--	0.9	1.0	1.0	0.2	0.2	0.2	--	--	--	0.6	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	574	575	575	575	575	575	575	575	575	575	575	575	575	575	575	575	577	574
Reactor Pressure, psig	103	596	596	596	595	594	299	299	101	600	600	600	103	103	102	102	597	594
Product Gas Rate, SCF/hr	1.51	1.71	1.56	1.54	0.92	0.98	3.65	3.67	3.70	3.12	2.91	1.54	3.35	1.62	0.84	0.83	1.25	1.23
Product Gas Composition, mole %																		
Nitrogen	--	0.5	--	--	--	0.6	--	0.7	0.5	0.5	0.1	--	--	--	--	0.4	--	0.6
Helium	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	5.1	2.3	2.0	1.8	1.5	1.2	3.5	3.7	3.0	6.6	6.6	2.9	6.3	4.5	3.0	2.8	5.5	9.0
Carbon Dioxide	0.7	0.3	0.3	0.4	0.4	0.4	0.2	0.1	0.1	0.4	0.3	1.8	1.0	1.5	2.1	1.8	0.2	0.1
Hydrogen	22.6	3.1	4.4	4.5	5.1	6.9	11.0	9.0	9.4	4.0	8.5	2.6	9.4	5.3	4.4	5.6	22.4	28.9
Methane	71.6	93.5	91.3	93.2	93.0	88.5	85.3	85.5	85.3	86.9	84.4	92.7	83.3	88.7	90.5	89.3	71.0	61.3
Ethane	--	0.1	0.1	0.1	--	0.1	--	0.1	0.1	0.1	0.1	--	--	--	--	0.1	--	0.1
Benzene	--	0.1	1.7	--	--	1.2	--	0.9	1.6	1.5	--	--	--	--	--	--	0.9	--
Cyclohexane	--	0.1	0.2	--	--	1.1	--	--	--	--	--	--	--	--	--	--	--	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	3.86	2.87	4.56	4.56	2.66	4.83	3.04	3.25	3.38	2.05	2.05	1.98	2.34	2.15	2.04	2.04	4.53	3.15
Water Collected, lb/hr x 10^4	39	308	209	143	451	55	77	165	49	71	24	33	55	60	104	132	328	--
Rate of CO Conversion, lb-mole/hr-g catalyst x 10^4	0.90	0.52	0.60	0.68	0.46	0.44	0.61	0.56	0.97	1.43	1.22	1.70	1.13	0.85	0.56	0.58	1.02	--

Table 5-35. METHANATION DATA-EFFECT OF EXCESS CO_2 ON METHANATION
(Union Carbide UC344-9 Catalyst)

Run No.	336	337	338	339	340
Catalyst Weight, g	2.3	2.3	2.3	2.3	2.3
Feed Gas Rate, SCF/hr	6.28	7.03	6.57	4.57	4.64
Feed Gas Composition, mole %					
Nitrogen	0.1	0.2	0.6	0.5	0.2
Helium	--	--	--	--	0.2
Carbon Monoxide	0.1	0.1	4.9	7.4	4.9
Carbon Dioxide	5.2	9.0	--	0.2	15.4
Hydrogen	94.4	90.6	--	29.3	14.0
Methane	0.2	0.1	94.2	62.4	65.1
Ethane	--	--	0.3	0.2	0.2
Total	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	429	583	579	598	598
Reactor Pressure, psig	655	605	660	615	620
Product Gas Rate, SCF/hr	6.15	6.41	6.50	4.14	4.30
Product Gas Composition, mole %					
Nitrogen	0.1	0.2	0.6	0.6	0.2
Helium	--	--	--	--	0.2
Carbon Monoxide	0.1	0.0	4.9	3.7	1.8
Carbon Dioxide	5.2	6.8	--	0.2	16.2
Hydrogen	94.4	90.0	--	74.2	74.1
Methane	0.2	3.0	94.2	74.2	74.1
Ethane	--	--	0.3	0.3	0.2
Total	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO_2 Ratio	18.1	10.1	0	3.96	2.86
Water Collected, lb/hr X 10^4	0	48	0	89	34
Rate of CO_2 Conversion, lbmol/hr-g cata. X 10^4	0	2.22	0	2.09	1.69

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Table 5-36. METHANATION DATA-EFFECT OF CO_2 AND N_2 ON METHANATION (Harshaw Ni 0104T)

Run No.	341a*	341b*	342	343†	344‡
Catalyst Weight, g	3.5	3.5	3.5	3.5	3.5
Feed Gas Rate, SCF/hr	5.87	5.87	5.02	4.02	4.04
Feed Gas Composition, mole %					
Nitrogen	63.5	63.5	0.7	88.5	84.1
Helium	1.7	1.7	--	--	--
Carbon Monoxide	--	--	1.3	1.6	--
Carbon Dioxide	18.3	18.3	20.8	0.0	0.8
Hydrogen	14.8	14.8	15.5	9.9	14.9
Methane	1.7	1.7	61.5	--	0.2
Ethane	--	--	0.2	--	--
Total	100.0	100.0	100.0	100.0	100.0
Reactor Temperature, °F	597	590	599	600	596
Reactor Pressure, psig	607	625	605	592	580
Product Gas Rate, SCF/hr	5.03	4.67	4.61	3.79	4.06
Product Gas Composition, mole %					
Nitrogen	62.9	63.1	0.7	92.0	84.9
Helium	2.0	2.1	--	--	--
Carbon Monoxide	--	0.9	0.2	0.0	--
Carbon Dioxide	20.5	22.6	22.4	0.2	0.1
Hydrogen	10.8	8.5	6.5	6.2	14.7
Methane	3.8	2.8	70.0	1.6	0.3
Ethane	--	--	0.2	--	--
Total	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO_2 Ratio	0.81	0.81	0.75	--	18.6
Water Collected, lb/hr X 10^4	196	196	65	24	0
Rate of CO_2 Conversion, lbmol/hr-g cata. X 10^4	0.32	0.14	0.42	0.48	0

* 0.12 wt % of NH_3 was found in the liquid product.

† 0.09 wt % of NH_3 was found in the liquid product.

‡ Temperature was increased to 700°F then dropped back to 596°F and carbon was deposited.

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Table 5-37. METHANATION DATA – CATALYST EVALUATION (Union Carbide UC466-34)

	345[a]	346	347	348[b]	349[c]	350[d]	351a	351b	351c	351d	351e	351f	351g	352
Catalyst Weight, g	3.6	2.5	2.5	2.5	2.5	2.5	4.6	4.6	4.6	4.6	4.6	4.6	4.6	4.6
Feed Gas Rate, SCF/hr	3.13	3.19	5.35	5.21	3.25	3.24	3.77	--	--	--	--	--	--	3.94
Feed Gas Composition, mole %														
Nitrogen	--	--	0.2	0.5	--	--	0.5							--
Helium	--	--	--	--	--	--	--							--
Carbon Monoxide	12.0	11.6	4.0	5.5	10.4	12.6	6.9							8.4
Carbon Dioxide	0.3	1.3	0.6	0.2	--	--	0.3							--
Hydrogen	86.9	85.6	30.4	21.0	89.6	87.4	30.9			Same Composition				33.2
Methane	0.3	1.5	64.8	72.7	--	--	61.2							58.4
Ethane +	0.5	--	0.2	0.1	--	--	0.2							--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0							100.0
Reactor Temperature, °F	296-701	585	600	610-1064	576	565	698	745	863	901	965	1027	767	1108
Reactor Pressure, psig	600	590	605	595	582	580	600	600	600	600	600	600	600	580
Product Gas Rate, SCF/hr	2.87	2.03	4.73	4.75	3.25	3.24	2.94	3.03	3.03	3.05	3.01	2.88	2.99	3.59
Product Gas Composition, mole %														
Nitrogen	--	--	0.3	0.5	--	--	0.6	0.5	0.5	0.5	0.5	0.3	0.3	--
Helium	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Carbon Monoxide	6.7	1.3	1.2	3.3	10.4	12.6	2.0	1.5	0.7	0.6	0.5	1.0	1.2	1.8
Carbon Dioxide	1.6	0.6	0.3	0.5	--	--	1.1	0.2	0.2	0.2	0.2	0.6	0.6	--
Hydrogen	87.4	76.3	19.7	14.9	89.6	87.4	17.3	17.3	17.3	16.8	14.4	17.2	15.2	20.0
Methane	3.6	21.7	78.2	80.6	--	--	79.9	80.3	81.1	81.7	84.2	80.8	82.5	78.2
Ethane	0.7	0.1	0.3	0.2	--	--	0.2	0.2	0.2	0.2	0.2	0.1	0.2	--
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Feed H_2/CO Ratio	7.24	7.38	7.60	3.82	8.6	6.9	4.5	4.5	4.3	4.5	4.5	4.5	4.5	3.95
Water Collected, lb/hr X 10^4	16	214	45	45	0	0	63	63	63	63	63	63	63	--
Rate of CO Conversion, lb/mol/hr-g catalyst X 10^4	1.77	4.07	1.63	0.88	0	0	1.14	1.21	1.36	1.37	1.39	1.30	1.26	1.50

[a] Catalyst deactivated rapidly. Analysis of catalyst afterwards showed changes of crystal structure. Starting temperature is too low for this pressure.

[b] Catalyst was subjected to temperature cycling between 610° and 1064°F.

[c] CSTR Reactor shaft was found to be loose.

[d] Catalyst was regenerated after exposed to air.

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Table 5-38. METHANATION DATA-EFFECT OF N_2 ON METHANATION (Harshaw Ni-0104T)

Run No.	353[a]	354	355[b]	356	357[c]	358[d]	359
Catalyst Weight, g	4.6	4.6	4.6	4.6	4.6	0.0	0.0
Feed Gas Rate, SCF/hr	3.05	3.54	5.08	5.95	6.26	5.70	5.18
Feed Gas Composition, mole %							
Nitrogen	9.3	22.7	37.9	21.4	22.2	22.8	23.8
Helium	0.1	0.1	--	--	--	--	--
Carbon Monoxide	4.7	3.1	2.5	--	--	--	--
Carbon Dioxide	1.2	1.1	0.92	--	--	--	--
Hydrogen	24.3	22.2	17.9	78.3	77.8	77.2	76.2
Methane	56.6	47.7	38.1	0.3	--	--	--
Ethane	2.7	2.2	1.8	--	--	--	--
Propane	0.78	0.67	0.56	--	--	--	--
n-Butane	0.16	0.08	0.25	--	--	--	--
i-Butane	0.09	0.08	0.05	--	--	--	--
Pentanes+[e]	0.07	0.07	0.02	--	--	--	--
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Reactor Temperature, °F	794	792	795	797	672	670	711
Reactor Pressure, psig	965	975	970	960	1010	1000	630
Product Gas Rate, SCF/hr	2.54	2.86	4.63	5.95	5.84	5.70	5.18
Product Gas Composition, mole %							
Nitrogen	10.7	28.6	40.0	21.4	22.2	22.8	23.8
Helium	0.07	0.04	--	--	--	--	--
Carbon Monoxide	0.29	0.42	0.52	--	--	--	--
Carbon Dioxide	0.37	0.40	0.46	--	--	--	--
Hydrogen	7.2	8.1	7.7	78.3	77.75	77.2	76.2
Methane	80.9	61.7	50.5	0.3	--	--	--
Ethane	0.34	0.46	0.49	--	--	--	--
Propane	0.08	0.16	0.16	--	--	--	--
n-Butane	0.02	0.07	0.11	--	--	--	--
i-Butane	0.01	0.03	0.04	--	--	--	--
Pentanes+[e]	0.02	0.02	0.02	--	--	--	--
Total	100.00	100.00	100.00	100.0	99.95	100.0	100.0
Feed H_2/CO Ratio	5.2	7.1	7.1	--	--	--	--
Water Collected, lb/hr X 10^4	207	33	59	0	0	0	0
Rate of CO Conversion, lb-mol/hr-g cata. X 10^4	0.76	0.55	0.58	0	0	0	0

[a] Feed gas contains 1.0 ppm C_2H_3SH.

[b] 0.002 g of NH_3 was found in 3.45 SCF of product gas, (0.003 mol % in product).

[c] 0.092 g of NH_3 was found in 8.45 SCF of product gas, (0.05 mol % in product).

[d] 0.0003 g of NH_3 was found in 3.13 SCF of product gas, (5 X 10^{-6} mol % in product).

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It was found that:

1) If both carbon monoxide and carbon dioxide are present in the feed, the carbon monoxide will be methanated first.

2) Water-gas shift reaction may compete with the carbon dioxide methanation reaction for some catalysts. In general, carbon dioxide will be hydrogenated to methane when the concentration of carbon monoxide is less than 0.2 mole percent.

3) Excess carbon dioxide (15% or more) may hinder the carbon monoxide methanation reaction.

5.5.9 Effect of Nitrogen on the Methanation Catalyst

As early as January, 1968 it was found that after making successful runs at 5 and 20 atmospheres total pressure, deactivation took place at 40 atmospheres, 575°F and approximately 10% CO, 30% H_2, 60% N_2 in the CSTR. This might have been caused by some N_2-H_2 reaction. The diluent was changed from nitrogen to helium and it was found that rates at similar conditions became higher. The matter was not investigated further at that time because no appreciable amount of nitrogen was expected in the HYGAS process.

During the year 1972-1973, the investigation of the effect of nitrogen on the methanation catalysts was started again because of the possibility that excess nitrogen in the methanator during start-up and shut-down for the HYGAS process could be a problem. Other coal gasification processes, where air is used, could indeed have a problem with excess nitrogen. It was found that:

1) The reactor wall (316ss) is a mild ammonia formation catalyst.

2) High-nickel content catalysts are mild ammonia formation catalysts in the absence of carbon oxides.

3) Ammonia is not likely to form when the concentration of nitrogen in the feed to the methanator is less than 50% of that for HYGAS conditions.

4) If ammonia is formed, it tends to deactivate the methanation reaction. The catalyst can be regenerated by passing hydrogen at about 700°F. However, carbon deposition may follow deactivation. The results can be seen in Tables 5-36 and 5-38.

Catalyst manufacturers have been informed about this behavior. They have experienced ammonia formation during start-ups, using the same catalyst for a different purpose. It did not affect their applications. For coal gasification, methane and various carbon oxides are present in the gas stream. It is also known that the methanator condition favors carbon deposition thermodynamically. Therefore, proper care should be taken if there is a large amount of nitrogen present. The equilibrium constants for methanation, the water-gas shift, and ammonia formation reactions are

presented in Figure 5-17. As can be seen, ammonia is not likely to form when there is carbon monoxide, not only because the nickel is a better catalyst for methanation, but also because the equilibrium favors the formation of methane. However, in the absence of carbon monoxide (and carbon dioxide) the equilibrium favors the formation of ammonia at lower temperatures and higher pressures. This behavior was verified by the experimental data.

5.5.10 Effect of Sulfur on the Methanation Catalysts

A total of eleven life-test type of runs were made to study the effect of H_2S on the life of catalysts. Two types of catalysts were used, the Harshaw Ni-0104T and the Union Carbide 204-41, in a packed bed reactor. The approach is to simulate the space velocity and the Reynolds number designed for the HYGAS plant. The experimental results are presented in Tables 5-39 and 5-40. It was found that:

1) Small concentrations (less than 1 ppm) of propyl mercaptan and thiophene poison the nickel catalysts slightly but it is tolerable. Methyl mercaptan, carbonyl sulfide and hydrogen sulfide poison the nickel catalysts quickly and intolerably.

2) Catalysts were poisoned quickly at hydrogen sulfide concentrations greater than 1.2 ppm in the feed.

3) Catalyst deactivation was more sudden than gradual.

4) Carbon was precipitated after the catalyst was poisoned. Analysis showed that although two-thirds of the catalyst bed was not poisoned by sulfur, carbon was deposited and plugged the reactor.

5) Sulfided catalysts were not regenerable,[3] nor were carbon-deposited catalysts regenerable.

5.5.11 Current Catalysis Studies at the Institute of Gas Technology

A number of the recently developed methanation catalysts, which are not reported here because of incomplete investigation, are being studied. These catalysts are:

Union Carbide UC964-34
Girdler G-87 promoted
Catalysts and Chemicals CCI C150-4-03
Mallinckrodt Ni237T
Harshaw ———

The results of these studies will be published at the appropriate time.

5.6 Methanation Rate Expression

A number of rate equations can be found in the literature and some of these have proposed mechanisms as well. Table 5-41 presents some of the published forms. The method of least squares was used to fit all

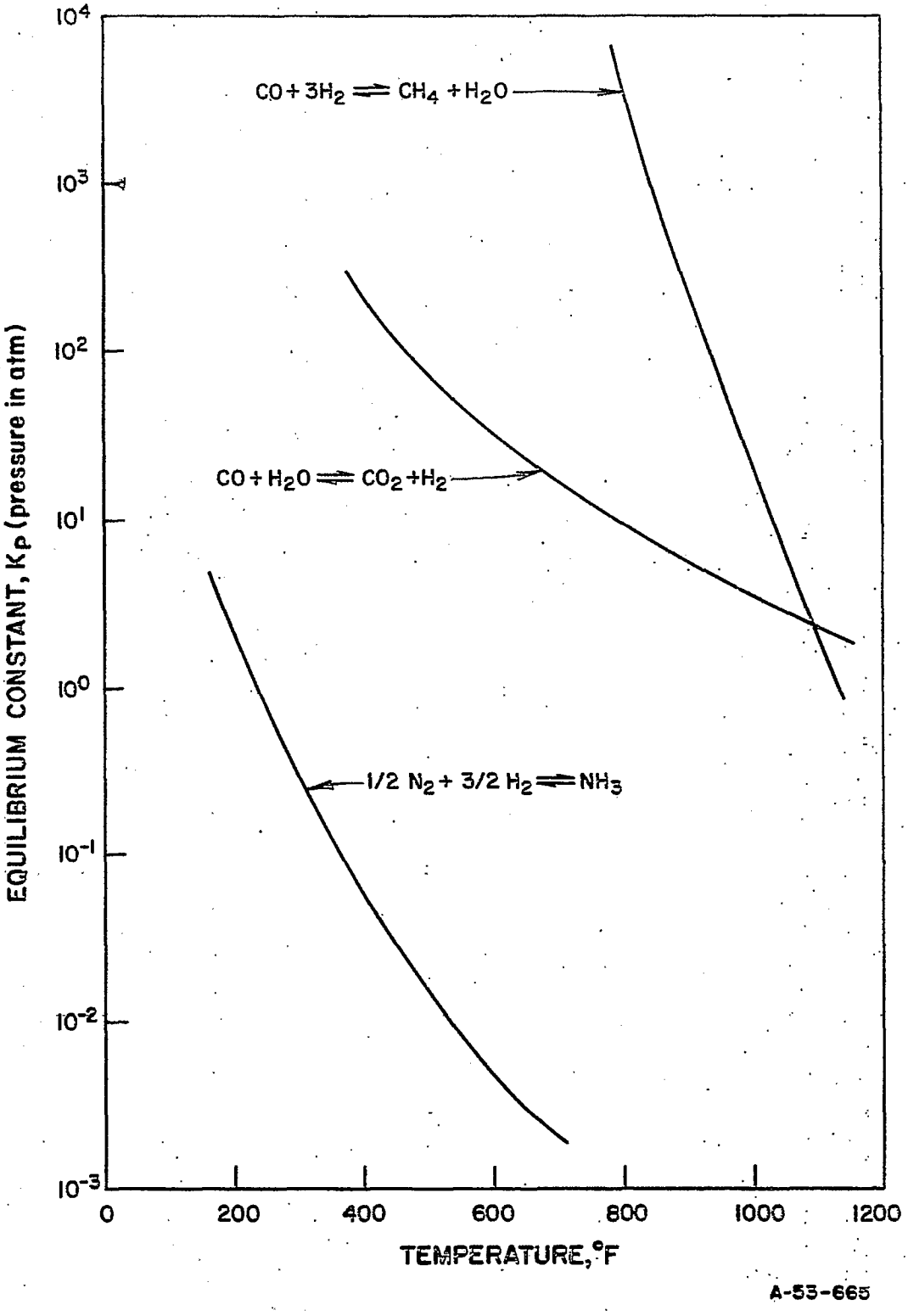

Figure 5-17. EQUILIBRIUM CONSTANTS FOR METHANATION, WATER-GAS SHIFT, AND AMMONIA FORMATION REACTORS

Table 5-39. LIFE STUDY OF METHANATION CATALYST IN THE PRESENCE OF H_2S (Catalyst: Harshaw Ni 0104-T, 1/8-in. pellets in packed bed)

Run No.	HS-1	HS-2	HS-3	HS-4	HS-5	HS-6	HS-6 (Cont)
Catalyst Weight, g	85.5	85.5	85.5	85.5	74.1	74.1	74.1
Reactor Pressure, psig	970	950	930	940	860	615	600
Reactor Temp.							
Top Zone, °F	550	270-565	240-600	195-725	240-710	660-710	375
Middle Zone, °F	720	710-758	720-760	410-720	735-800	735-740	760
Bottom Zone, °F	564	575-800	570-750	575-825	830-910	744-925	810-930
Feed Gas Composition, mole %							
Hydrogen	14.9	14.2	14.3	14.3	18.4	18.6	18.6
Methane	77.8	76.5	77.5	77.5	61.1	72.8	72.8
Carbon Monoxide	4.1	3.9	3.1	3.1	3.2	3.4	3.4
Carbon Dioxide	0.6	0.5	0.5	0.5	0.4	0.5	0.5
Nitrogen	--	2.8	2.3	2.3	14.8	2.3	2.3
Argon	0.04	0.01	0.01	0.01	0.07	0.05	0.05
Ethane	2.6	2.1	2.1	2.1	2.0	2.3	2.3
Propane	--	--	0.11	0.11	--	--	--
Total	100.04	100.01	99.92	99.92	99.97	99.95	99.95
Feed Gas Rate, SCF/hr	17.13	19.43	19.12	16.59	18.12	3.17	3.17
Feed Sulfur Content, ppm	0.0	0.0	0.6	1.2	2.9	4.5	4.5
Product Composition, mole %							
Hydrogen	1.0	1.0	--	--	12.9	5.0	5.3
Methane	95.3	95.3	--	--	82.4	92.5	91.0
Carbon Monoxide	0.0	0.0	0.0	1.1	0.1	0.0	0.2
Carbon Dioxide	0.7	0.7	--	--	0.7	0.1	0.8
Nitrogen	3.0	3.0	--	--	3.7	2.3	2.3
Argon and Helium	0.01	0.01	--	--	0.11	0.07	0.41
Ethane	0.0	0.0	--	--	0.1	0.0	--
Propane	--	--	--	--	--	--	--
Total	100.01	100.01	--	--	100.01	99.97	100.01
Product Gas Rate, SCF/hr	12.42	--	16.81	18.11	15.90	2.41	1.11
Product Sulfur, ppm	0.0	0.0	--	0.17	0.0	0.0	1.9
Water Productd, lb/hr	--	--	0.040	0.045	0.038	--	0.007
Space Velocity, $\frac{SCF/hr}{cu\ ft}$	7358	7942	7689	6396	8547	1496	1496
Total Run Time, hr	1.33	2.67	6.00	71.2	24	77.3	151.8
CO Converted, mol %	100	100	100	61.3	97.3	100	97.9

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Table 5-40. LIFE STUDY OF METHANATION CATALYST IN THE PRESENCE OF H_2S

Run No,	Ni0104T, 1/4"		UC204-41, 1/8"		
	HS-7	HS-8	HS-9	HS-10	HS-11
Catalyst Weight, g	63.0	51.0	46.0	47.7	48.3
Reactor Pressure, psig	1000	1000	800	780	800
Reactor Temperature, °F					
Top Zone	210-570	535-790	500-813	503-672	613-680
Middle Zone	560-740	805-930	215-920	626-796	690-730
Bottom Zone	730-800	930-975	252-518	480-750	420-750
Feed Gas Composition, mol %					
Hydrogen	18.2	16.8	17.1	17.1	17.1
Methane	70.0	71.3	65.9	65.9	65.9
Carbon Monoxide	4.7	4.2	1.1	4.1	4.1
Carbon Dioxide	0.44	0.17	0.5	0.5	0.5
Nitrogen	2.4	2.8	2.2	2.2	2.2
Argon and Helium	--	0.08	6.0	6.0	6.0
Ethane	3.1	3.2	3.1	3.1	3.1
Propane	1.09	1.11	0.7	0.7	0.7
Total	99.93	99.96	99.6	99.6	99.6
Feed Gas Rate, SCF/hr	17.89	17.43	15.02	19.10	18.78
Feed Sulfur Content, ppm	12.0	1.6	1.3	3.6	4.3
Product Gas Composition, mol %					
Hydrogen	8.4	5.2	12.1	--	--
Methane	83.0	90.8	78.6	98.0	98.0
Carbon Monoxide	2.7	0.2	2.7	0.2	--
Carbon Dioxide	0.49	1.3	0.9	0.1	--
Nitrogen	1.8	2.3	2.6	--	--
Argon and Helium	0.1	0.08	0.4	--	--
Ethane	2.6	0.12	2.0	--	--
Propane	0.86	0.01	0.5	--	--
Total	99.95	100.01	99.8	--	--
Product Gas Rate, SCF/hr	16.61	13.76	8.74	18.89	18.28
Product Sulfur, ppm	0.7	0.1	0.1	--	--
Water Produced, lb/hr	0.057	0.014	0.006	--	0.002
Space Velocity, SCF/hr-cu ft	9.925	11.944	10.781	13.223	12.841
Total Run Time, hr	4.7	40	242	2	64
CO Converted, mol %	46.8	96.3	61.7	95.1	72.0

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Table 5-41. RATE EQUATIONS FOR METHANATION PROPOSED BY VARIOUS INVESTIGATORS

Author(s)*	Rate Equation	Range Temperature, Pressure	Remarks
Nicolai et al	$r = k p_{H_2}^{3.3} / p_{CO}^{0.2}$	250°-300°C, 0.1-1.0 atm	This work is concentrated on CO_2 hydrogenation on a nickel catalyst. Very little work is done on CO methanation.
Akers and White	$r = \frac{p_{CO} p_{H_2}^3}{(A + Bp_{CO} + Dp_{CO_2} + Ep_{CH_4})}$	300°-350°C, 1 atm	A reduced nickel catalyst was used. The water-gas shift reaction was also studied and a rate equation for the formation of CO_2 was discussed.
Pursley et al.	$r_o = \frac{1.1\, p_{CO} p_{H_2}^{0.5}}{1 + 1.5\, p_{H_2}}$	500°-700°F, 14.7-400 psia	A nickel catalyst was used to study the initial rate of the CO-H_2 reaction. This equation was derived by using sulfur-free mixtures of CO and H_2 containing less than 30 mole % CO.
McKee	$r = k\, p_{H_2}^{1.33} / p_{CO}^{0.13}$	220°C, 21.4 atm	Platinum group metals were used as catalysts for the reaction: $2CO + 2H_2 = CH_4 + CO_2$.
Barkley et al.	$r = \frac{k\left[p_{CO_2} p_{H_2} - \frac{p_{CO} p_{H_2O}}{K}\right]}{1 + K_A p_{CO_2} + K_R p_{CO}}$	1000°F	A study of the gas-phase reaction $CO_2 + H_2 = CO + H_2O$ over an iron-copper catalyst. A mechanism for this reaction was postulated.
Binder and White	$r = \frac{C_1 (p_{CO_2} p_{H_2}^2 - \frac{p_{CH_4} p_{H_2O}^2}{K_1 p_{H_2}^2})}{(p_{H_2}^{0.5} + C_2 p_{CO_2} + C_3)}$	500°-750°F, 1 atm	A reduced nickel catalyst was used.
Binder and White	$r = \frac{C_1 (p_{CO_2} p_{H_2}^4 - \frac{p_{CH_4} p_{H_2O}^2}{K_1 p_{H_2}^2})}{(p_{H_2}^{0.5} + C_2 p_{CO_2} + C_3)^4}$	500°-750°F, 1 atm	A reduced nickel catalyst was used.
Weller	$r = k\, p_{CO}\, p_{H_2}^{0.5}$	See Weller's work, listed in Bibliography	Used Akers and White's data and arrived at this simpler rate expression which correlates rate data with about the same accuracy. Excellent discussion on the analysis of data.
Schoubye	$r = \frac{Z_1 \exp\left[-E_1/RT\right] p_{H_2}^n}{\left[1 + Z \exp(16650/RT)(p_{CO}/p_{H_2})^{-1.5}\right]}$	200°-300°C, 2-15 atm	Nickel catalysts were used. Order of CO was found to be from 0 to −0.5.
Wen et al.	$r = k\, p_{CO}^{0.7}\, p_{H_2}^{0.3}$	550°-850°F, 14.7-1000 psia	IGT data were used in this analysis.
Tajbl	$r = 7.85 \times 10^3 \exp\left(-\frac{17300}{RT}\right) X_{CO}^{0.62}$	550°-600°F, 69 atm	Initial analysis of effluent gas mixture from hydrogasifier.
Lee, A. L.	$r = \frac{k_1 p_{CO} p_{H_2}^{0.5}}{1 + k_2 p_{H_2} + k_3 p_{CH_4}}$	550°-850°F, 14.7-1000 psia 500°-900° F, 14.7-1000 psia	Analysis of feed gas mixtures of H_2-CO; H_2-CO-He; H_2-CO-CH_4; and H_2-CO-CH_4-CO_2-C_6H_6. This study.

* For details of any work mentioned above, see work listed alphabetically by author, in Bibliography.

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the data obtained in the period reported. The data from the catalyst poison studies are not used for the rate analysis. The rate expression is:

$$r = \frac{kP_{CO}P_{H_2}^{0.5}}{1 + 0.1P_{H_2} + 0.05P_{CH_4}}$$

where

r = rate of methane formation, $\frac{\text{lb mole}}{\text{hr-g catalyst}} \times 10^{-4}$

$k = Ae^{-E/RT}$

$A = 1.06 \times 10^{-2}$

$E = 1.25 \times 10^{4}$ Btu/lbmole (6.9 Kcal/gmole)

$R = 1.987$ Btu/lbmole—°R

T = temperature in °R

This rate expression is suitable for relatively high nickel-content methanation catalysts of 0.25-inch size. It is applicable for all pressures and within the temperature range of 525° to 900°F. The rates are very low at temperatures lower than 525°F. This rate equation will not apply for the following conditions:

1) Feed gas containing more than 1.5% benzene.
2) Feed gas containing more than 0.5 ppm of hydrogen sulfide.
3) Feed gas containing more than 2 ppm mercaptans.
4) Feed gas containing more than 5% water.
5) Feed gas containing more than 20% carbon dioxide.
6) Feed gas containing more than 50% nitrogen.
7) Feed gas containing ammonia, phenol and hydrogen cyanide.
8) Feed gas with a hydrogen-to-carbon monoxide ratio less than 2.85.

5.7 Catalyst Life Studies

At the beginning of this research, no successful work had been reported on fixed-bed methanation of high carbon monoxide, high methane content gases with commercial nickel catalysts. In packed-bed methanation reactors, the high exothermic heat of reaction may cause catalyst deactivation through hot spots and carbon deposition. For each catalyst tested, a life test of about 90 hours was run in the CSTR. For each of these catalysts which demonstrated good activity, good high- and low-temperature limits, good thermal resistance and relatively low cost, a special life test was conducted in a packed-bed reactor of 0.5 to 1.25 inches diameter. During these tests, all the process variables (such as temperature, pressure,,flow-rate, composition and steam-to-gas ratio) were varied. The temperature distribution in the reactor was recorded with the start-up temperatures, the pressure effect on the yield was recorded with pressure changes, and several start-up and shut-down procedures were studied. The physical properties of the catalysts were analyzed before and after the test (if no secrecy agreement was involved) for changes in surface area, crystal structure, carbon content, nickel content, sulfur content, and crushing strength.

Three of the catalysts subjected to this treatment are reported here. Other catalysts, mostly newly developed ones, which have been or are being studied, will be reported in the future. The catalysts reported here are Girdler G-65, Harshaw Ni-0104T, and Union Carbide UC681-74.

5.7.1 Girdler G-65 Catalyst

The results of the life study on G-65 catalyst are presented in Tables 5-42 to 5-44. There was sufficient hydrogen in the feed to completely methanate both carbon monoxide and carbon dioxide. The results show that at the low space velocities both the carbon monoxide and carbon dioxide were almost completely reacted and the 0.8 percent of ethane in the feed was completely hydrogenated. A plot of temperature at various locations in the catalyst bed versus time on stream is shown in Figure 5-18. The plot shows that, at this operating condition, the conversion was steady. The space velocity was increased in Run LT-7 and dropped slightly in Run LT-8. Both runs were stopped when the carbon deposition was suspected as the reason for the deactivation. In Run LT-7, the top of the bed contained about 6 percent carbon by weight and in Run LT-8, about 8 percent. There was also an increase in the sulfur content of the catalyst after the run.

5.7.2 Harshaw Ni-0104T Catalyst

Harshaw Ni-0104T catalyst was used in life study LT-11. The results are presented in Table 5-45. The space velocity was varied from 2539 to 9130 standard cubic feet per hour per cubic foot during the run. Carbon monoxide and ethane were at equilibrium conversion at all space velocities. Carbon dioxide breakthrough was noticed at the higher space velocities. A bed of activated carbon and zinc oxide at 300°F reduced the sulfur content of the feed gas from about 2 ppm to less than 0.1 ppm, so there was no reason for the catalyst deactivation by sulfur poisoning. The operating temperature was much lower than that for G-65; therefore, there was no carbon deposition problem for this run. The physical strength of this already weak catalyst was decreased at the end of the run.

5.7.3 Union Carbide UC 681-74 Catalyst

The first zeolite-based catalyst tested was a Union Carbide Linde 8 percent nickel on NaX on March 16, 1971. It was found that this catalyst has approximately the same activity as others based on the nickel content of the catalysts, but has shown some potential for both high-temperature resistance and better physical strength. Since then, Union Carbide has submitted four sets of zeolite-based catalysts for evaluation as a methanation catalyst. These catalysts are UC 204-41, UC 344-9, UC 466-34, and UC 681-74. Extensive evaluation tests were performed for these catalysts. UC 466-34* catalyst has the following qualities:

1) Its activity is among the top 5 percent of all the catalysts tested.

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* Same as catalyst UC 681-74.

Table 5-42. METHANATION LIFE TEST, RUN LT-6

Run No.	LT-6				
Catalyst	G-65				
Catalyst Volume, cu ft	0.0327				
Test Duration, hr	64	160	208	361	412
Pressure, psig	999	998	997	1045	1015
Temperature, °F					
Preheater	615	600	605	640	640
7 in. from Top	1000	1010	1000	1005	1010
13 in. from Top	865	840	840	905	895
Product Gas	425	425	430	420	420
Furnace	570	550	550	570	570
Feed Gas Composition (Dry), mole %					
CO	12.6	12.6	12.6	12.4	12.4
CO_2	2.9	2.9	2.9	2.9	2.9
H_2	55.0	55.0	55.0	57.1	57.1
CH_4	27.0	27.0	27.0	25.1	25.1
C_2H_6	0.8	0.8	0.8	0.8	0.8
N_2	1.65	1.65	1.65	1.7	1.7
Total	99.95	99.95	99.95	100.0	100.0
Space Velocity, SCF/cu ft-hr	280	281	282	296	299
Feed Rate, SCF/hr	9.18	9.19	9.22	9.68	9.79
Product Gas Composition (Dry), mole %					
CO	0.0	0.0	0.0	0.0	0.0
CO_2	0.3	0.1	0.1	0.1	0.1
H_2	3.5	4.2	4.8	5.4	5.2
CH_4	93.9	93.7	93.1	92.5	92.5
C_2H_6	0.0	0.0	0.0	0.0	0.0
N_2	2.3	2.04	2.02	2.0	2.19
Total	100.0	100.04	100.02	100.0	99.99
Product, SCF/SCF feed	0.537	0.520	0.502	0.499	0.510
Heating Value, Btu/SCF	961.9	962.1	958.0	953.9	953.2
Carbon Recovery, %	115.0	111.3	105.6	109.3	112.9
Hydrogen Recovery, %	108.5	108.1	103.3	104.6	104.5
Oxygen Recovery, %	99.0	112.6	105.9	109.0	96.5
Water Collected by Condensate Measurement, g/hr	35.4	40.88	37.6	41.40	36.9
CO Conversion, %	100.0	100.0	100.0	100.0	100.0
CO_2 Conversion, %	94.4	98.2	98.2	98.2	98.2
C_2H_6 Conversion, %	100.0	100.0	100.0	100.0	100.0

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Table 5-43. METHANATION LIFE TEST, RUN LT-7

Run No.	LT-7			
Catalyst	G-65			
Catalyst Volume, cu ft	0.00317			
Test Duration, hr	20	102	126	150
Pressure, psig	1002	993	996	998
Temperature, °F				
Preheater	850	875	950	945
7 in. From Top	1005	1025	1000	1000
14 in. From Top	825	825	950	975
22 in. From Top	700	715	910	925
Furnace	935	935	930	930
Feed Gas Composition (Dry), mole %				
CO	12.7	12.7	12.5	12.5
CO_2	3.2	3.2	3.2	3.2
H_2	57.5	57.5	56.9	56.9
CH_4	24.3	24.3	24.9	24.9
C_2H_6	1.0	1.0	1.3	1.3
N_2	1.26	1.26	1.2	1.2
Total	99.06	99.96	100.0	100.0
Space Velocity, SCF/cu ft-hr	3104	3091	3107	3129
Feed Rate, SCF/hr	9.84	9.80	9.85	9.92
Product Gas Composition (Dry), mole %				
CO	2.4	4.5	11.4	12.0
CO_2	0.7	1.3	2.8	3.3
H_2	16.1	25.3	54.6	56.2
CH_4	78.5	66.3	28.8	25.5
C_2H_6	0.2	0.4	1.1	1.2
N_2	2.11	2.19	1.33	1.84
Total	100.01	99.99	100.03	100.04
Product/Feed Ratio, SCF/SCF	0.41	--	0.97	--
Heating Value, Btu/SCF	837	749	509	490
Carbon Recovery, %	80.3	--	101.7	--
Hydrogen Recovery, %	81.3	--	104.0	--
Oxygen Recovery, %	95.3	--	102.3	--
Water Collected by Condensate Measurement, g/hr	36.7	--	6.01	--
CO Conversion, %	92.2	--	6.01	1.0
CO_2 Conversion, %	90.9	--	14.9	--
C_2H_6 Conversion, %	93.7	--	17.9	--

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Table 5-44. METHANATION LIFE TEST, RUN LT-8

Run No.	LT-8				
Catalyst	G-65				
Catalyst Volume, cu ft	0.00423				
Test Duration, hr	28	52	76	118	140
Pressure, psig	1002	997	982	1007	1008
Temperature, °F					
Preheater	595	595	595	595	595
9 in. From Top	940	925	885	900	835
18 in. From Top	735	735	715	725	685
28 in. From Top	665	670	665	650	640
Lower Furnace	685	685	685	675	660
Feed Gas Composition (Dry), mole %					
CO	12.8	12.8	12.8	12.6	12.6
CO_2	3.0	3.0	3.0	2.9	2.9
H_2	56.5	56.5	56.5	56.8	56.8
CH_4	25.4	25.4	25.4	25.3	25.3
C_2H_6	1.2	1.2	1.2	1.4	1.4
N_2	1.13	1.13	1.13	1.02	1.02
Total	100.03	100.04	100.04	100.04	100.03
Product/Feed Ratio, SCF/SCF	0.51	0.512	0.523	0.661	0.703
Heating Value, Btu/SCF	808	793	768	741	634
Carbon Recovery, %	91.1	90.7	88.6	107.8	80.1
Hydrogen Recovery, %	90.0	90.5	89.4	103.9	96.4
Oxygen Recovery, %	93.6	104.2	102.4	101.5	106.0
Water Collected by Condensate Measurement, g/hr	30.3	33.3	30.6	27.0	21.7
CO Conversion, %	86.0	81.6	80.0	70.6	50.9
CO_2 Conversion, %	83.0	81.2	79.2	68.0	49.0
C_2H_6 Conversion, %	78.7	78.6	78.2	57.4	54.7

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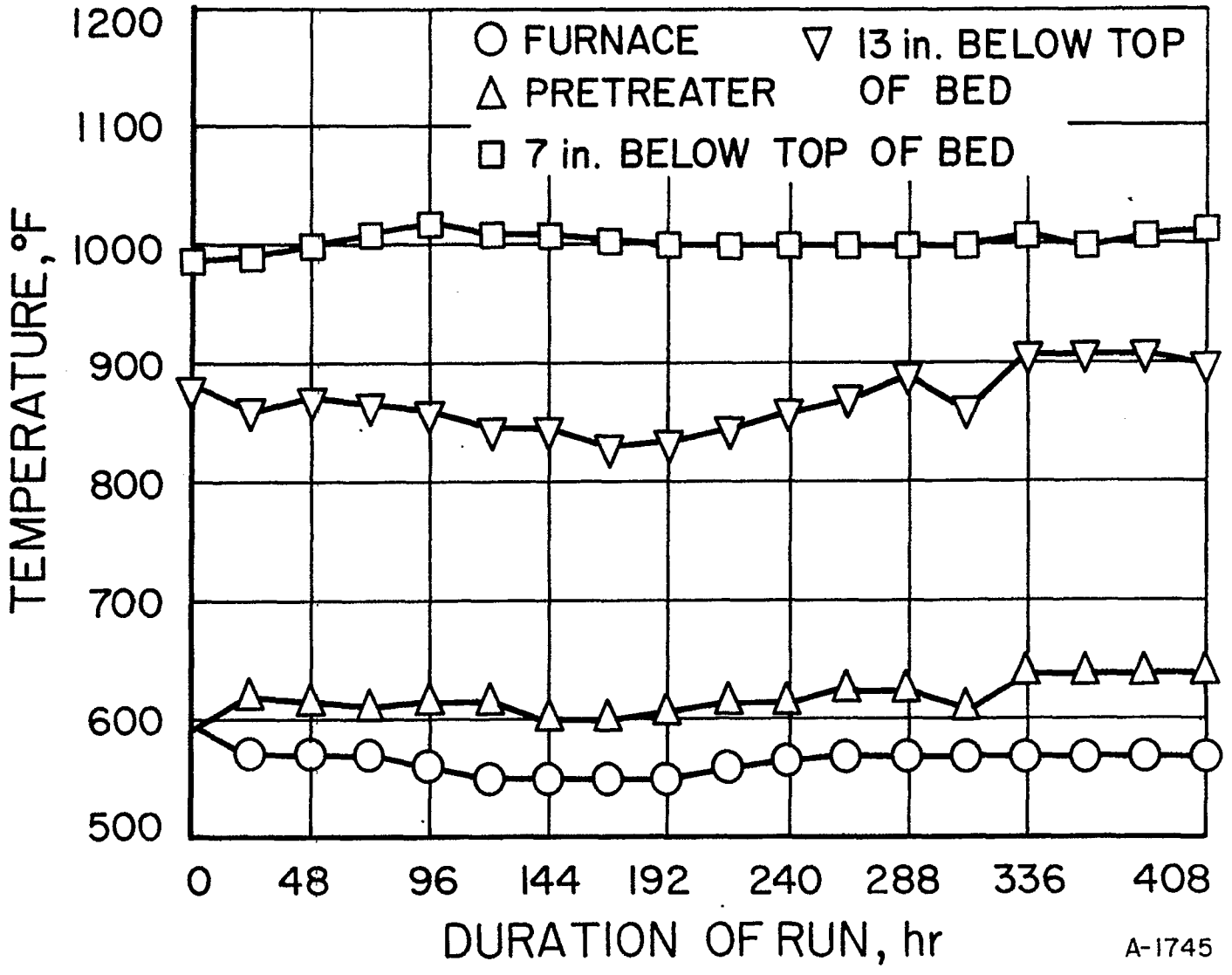

Figure 5-18. REACTOR TEMPERATURES

Table 5-45. METHANATION LIFE TEST, RUN LT-11

Run No.	LT-11								
Catalyst	Harshaw Ni-0104T								
Catalyst Volume, cu ft	0.00352								
Test Duration, hr	19	80	217	288	421	464	558	653	771
Pressure, psig	1000	1005	1003	1000	1006	1000	1000	1003	998
Temperature, °F									
Preheater	655	640	630	625	605	435	545	465	490
1-1/2 in. From Top	710	700	695	685	665	500	600	535	515
4 in. From Top	855	880	875	870	890	840	840	840	790
Product Gas	635	635	630	620	605	580	545	620	485
Furnace	585	580	575	550	450	495	495	480	425
Feed Gas Composition (Dry), mole %									
CO	4.3	4.0	4.0	3.5	4.0	4.0	4.0	4.0	3.7
CO_2	1.5	1.4	1.4	1.0	0.8	0.8	0.8	0.8	0.7
H_2	18.8	19.4	19.4	18.8	20.1	20.1	20.1	21.3	21.3
CH_4	70.1	69.3	69.3	70.0	69.0	69.0	69.0	68.0	68.0
C_2H_6	2.7	2.7	2.7	3.4	3.7	3.7	3.7	3.7	3.7
N_2	2.62	3.22	3.22	3.25	2.39	2.39	2.39	2.56	2.56
Total	100.02	100.02	100.02	99.95	99.99	99.99	99.99	99.96	99.96
Space Velocity, SCF/cu ft-hr	2539	2590	2599	2596	2619	4704	2551	4798	2619
Feed Rate, SCF/hr	8.99	9.12	9.15	9.14	9.22	16.56	8.34	16.89	9.24
Product Gas Composition (Dry), mole %									
CO	0.2	0.1	0.2	0.1	0.1	0.0	0.1	0.1	0.1
CO_2	0.9	1.0	1.0	0.8	0.6	0.1	0.2	0.1	0.1
H_2	1.8	1.8	1.7	1.4	1.5	1.6	1.5	2.1	3.3
CH_4	93.6	93.5	93.6	94.4	94.2	94.9	95.0	94.3	92.9
C_2H_6	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.1	0.4
N_2	3.34	3.53	3.33	3.12	3.4	3.29	3.07	3.25	3.17
Total	100.04	100.03	100.03	100.02	100.00	99.99	99.97	99.95	99.97
Product, SCF/SCF feed	0.77	0.77	0.77	0.78	0.78	0.82	0.64	0.80	0.88
Heating Value, Btu/SCF	942	940	941	948	950	955	957	947	949
Carbon Recovery, %	90.8	92.1	92.6	92.6	92.2	96.3	76.6	97.6	103.7
Hydrogen Recovery, %	91.3	91.5	92.0	90.9	91.5	96.3	76.3	94.0	102.9
Oxygen Recovery, %	94.5	97.8	101.8	90.5	109.8	100.9	81.7	105.7	114.5
Water Collected by Condensate Measurement, g/hr	10.40	9.88	10.37	7.26	10.24	19.62	8.34	19.00	11.15
CO Conversion, %	96.3	98.0	96.1	97.7	98.0	100.0	98.3	97.8	97.6
CO_2 Conversion, %	53.4	44.4	44.3	37.0	41.0	89.7	83.8	88.5	87.3
C_2H_6 Conversion, %	94.2	97.1	94.2	95.3	95.7	97.7	98.2	97.8	90.4

Run No.	LT-11							
Catalyst	Harshaw Ni-0104T							
Catalyst Volume, cu ft	0.00352							
Test Duration, hr	820	986	1109	1152	1250	1320	1391	1420
Pressure, psig	1014	1005	1003	1000	1006	1006	1000	1010
Temperature, °F								
Preheater	480	450	505	480	565	470	535	515
1-1/2 in. From Top	545	510	565	550	625	540	600	595
4 in. From Top	810	740	810	770	900	730	855	795
Product Gas	625	610	650	715	640	770	645	825
Furnace	480	470	5151	525	540	540	525	600
Feed Gas Composition (Dry), mole %								
CO	3.8	4.2	3.7	3.7	3.7	3.7	3.7	3.7
CO_2	0.6	0.6	0.8	0.8	1.0	1.0	1.0	1.0
H_2	19.8	20.0	18.9	18.9	19.6	19.6	19.6	19.6
CH_4	71.9	72.2	72.6	72.6	71.7	71.7	71.7	71.7
C_2H_6	1.2	1.1	0.9	0.9	0.9	0.9	0.9	0.9
N_2	2.73	1.94	3.09	3.09	3.06	3.06	3.06	3.06
Total	100.03	100.04	99.99	99.99	99.96	99.96	99.96	99.96
Space Velocity, SCF/cu ft-hr	4803	5284	4832	6852	4193	8664	4383	9130
Feed Rate, SCF/hr	16.91	18.60	17.01	24.12	14.76	30.50	15.43	32.14
Product Gas Composition (Dry), mole %								
CO	0.1	0.1	0.00	0.1	0.1	0.1	0.1	0.1
CO_2	0.00	0.00	0.1	0.1	0.1	0.3	0.2	0.5
H_2	2.8	4.2	3.0	3.3	2.6	3.3	2.4	4.0
CH_4	93.9	92.5	93.3	92.9	93.4	92.6	93.3	91.5
C_2H_6	0.00	0.00	0.00	0.00	0.1	0.00	0.00	0.00
N_2	3.16	3.16	3.55	3.56	3.66	3.74	4.03	3.89
Total	99.96	99.96	99.95	99.96	99.96	100.04	100.03	99.99
Product, SCF/SCF feed	0.86	0.84	0.82	0.82	0.82	0.80	0.83	0.80
Heating Value, Btu/SCF	952	940	949	944	941	932	938	922
Carbon Recovery, %	103.4	98.6	98.1	97.6	99.3	95.9	100.3	94.4
Hydrogen Recovery, %	101.8	97.7	96.8	96.5	96.9	94.2	97.5	93.0
Oxygen Recovery, %	105.5	78.8	84.9	90.5	67.3	81.5	65.0	89.8
Total Material Recovery, %	103.0	98.6	96.9	96.8	96.7	94.8	98.0	94.3
Water Collected by Condensate Measurement, g/hr	18.96	16.80	15.98	23.69	11.67	26.89	10.97	24.47
CO Conversion, %	97.3	97.9	100.0	97.7	97.7	97.8	97.7	97.8
CO_2 Conversion, %	100.0	100.0	89.6	89.6	91.7	75.7	81.3	59.8
C_2H_6 Conversion, %	100.0	100.0	100.0	100.0	89.6	100.0	100.0	100.0

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2) It has an upper temperature limit of 1140°F in the absence of steam.

3) It has a lower temperature limit of 550°F at 1000 psig. (The lower temperature limit is a function of pressure.)

4) It does not deactivate continuously under normal operating conditions.

5) It deactivated steadily in the presence of 1.3 ppm hydrogen sulfide.

This catalyst was considered worthy of a life study.

The catalyst was reduced according to Union Carbide's start-up procedure. The reactor was first purged with nitrogen for 2 hours followed by hydrogen at a flow rate of about 3 standard cubic feet per hour for 2 hours. The pressure in the reactor was gradually increased to 360 psig while heating up. The rate of heating was 100°F per hour until it reached 750°F. The reactor was held at 750°F for 12 hours while hydrogen was passed through at about 0.5 standard cubic feet per hour. The temperature was then lowered to 500°F and stabilized.

The feed was introduced at a space velocity of about 10,000 standard cubic feet per hour per cubic foot. The carbon oxides in the product gas were continuously monitored by the infrared analyzers, and conversions were observed immediately and at the end of 3 hours. Ninety-five percent of CO, 82 percent carbon dioxide, and 94 percent propane were converted (Run 1 in Table 5-46). The carbon monoxide methanation reaction and the carbon dioxide mathanation reaction are competing reactions. Usually the carbon dioxide will not be methanated until almost all of the carbon monoxide has been converted. Therefore, one may safely assume that when carbon dioxide in the feed is being methanated, the carbon monoxide has nearly all been converted.

All of the carbon monoxide in the feed was converted at the end of 4 hours. This run was continued for 117 hours; the only change was in feedwater concentration, from 3 to 1.5%. This change was to determine whether carbon deposition is a problem at this operating condition. There was no problem (Run 2 in Table 5-6).

Space velocity was doubled to 20,000 standard cubic feet per hour per cubic foot. At the end of 171 hours (55 hours at this space velocity), there was no change in conversion (Run 3 in Table 5-46). This run was made to find out the performance of the catalyst at nonequilibrium conditions or the breakthrough point. Although the breakthrough point was not reached at this flow rate, it was very close because of the sharp decrease in carbon dioxide conversion. While maintaining the space velocity at about 20,000 standard cubic feet per hour per cubic foot, the lower temperature limit was tested. The furnace temperature was decreased to 490°F, which in turn caused the reactor bed temperature to drop to 584°F. At the end of 236 hours, or after 34 hours at 490°F, 0.3 percent of carbon monoxide was found in the product and none of the carbon dioxide in the feed was converted

Table 5-46. Part 1. LIFE STUDY DATA FOR CATALYST UC 681-74, 1/8-INCH EXTRUSION

Run No.	1		2		3	
	Time, hr					
	3		117.5		171	
Analysis	Dry	Wet	Dry	Wet	Dry	Wet
Reactor Pressure, psig	355	355	355	355	360	360
Reactor Temp, °F	500	500	500	500	500	500
Top Zone No. 11	573	573	613	613	607	607
Bottom Zone No. 6	606	606	639	639	602	602
Feed Gas Flow Rate, SCF/hr	5.5962	5.7549	11.5527	11.7101	11.5527	11.7909
Feed H_2O Rate, lb-mol./hr	0.00043	0.00043	0.00043	0.00043	0.00064	0.00064
Feed Composition, mol %						
H_2	19.3	18.7	19.3	19.0	19.3	18.9
CH_4	68.7	66.9	68.7	67.7	68.7	67.3
CO	2.7	2.6	2.7	2.7	2.7	2.6
CO_2	2.6	2.5	2.6	2.6	2.6	2.5
N_2	2.4	2.3	2.4	2.4	2.4	2.4
C_2H_{6+}	2.9	2.8	2.9	2.9	2.9	2.8
C_3H_8	1.28	1.2	1.28	1.2	1.28	1.2
He	0.07	0.05	0.07	0.06	0.07	0.07
H_2O	--	2.95	--	1.44	--	2.23
Total	99.95	100.00	99.95	100.00	99.95	100.00
Product Gas Flow Rate, SCF/hr	4.1296	4.4425	8.8890	9.1986	8.7764	9.5645
Product H_2O Rate, lb-mol./hr	0.00081	0.00081	0.00081	0.00081	0.00204	0.00204
Product Composition, mol%						
H_2	1.0	0.95	1.0	0.9	1.1	1.0
CH_4	94.9	88.2	93.0	89.9	88.7	81.4
CO	0.2	0.17	0.0	0.0	0.0	0.0
CO_2	0.64	0.6	1.9	1.8	3.2	2.9
N_2	2.6	2.4	3.1	2.9	2.6	2.4
C_2H_{6+}	0.43	0.4	0.84	0.8	3.2	2.9
C_3H_8	0.11	0.08	0.08	0.08	1.12	1.0
He	0.08	0.08	0.09	0.08	0.11	0.1
H_2O	--	7.12	--	3.54	--	8.3
Total	99.96	100.00	100.01	100.00	100.03	100.0
Component Consumed, lb-mol./hr (% change)						
CO	0.00037 (95%)	--	0.00081 (100%)	--	0.00081 (100%)	--
CO_2	0.00031 (82%)	--	0.00034 (43%)	--	0.00005 (6%)	--
H_2	0.00269 (96%)	--	0.00556 (96%)	--	0.00554 (96%)	--
C_2H_{6+}	0.00037 (88%)	--	0.00068 (78%)	--	0.00014 (16%)	--
C_3H_8	0.00017 (94%)	--	0.00036 (95%)	--	0.000125(33%)	--
H_2O Produced, lb-mol./hr	0.000387	--	0.00038	--	0.00140	--
CH_4 Produced, lb-mol./hr	0.00019	--	0.00086	--	--	--
Space Velocity, SCF/hr-cu ft	--	10,738	--	21,850	--	21,994

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Table 5-46. Part 2. LIFE STUDY DATA FOR CATALYST UC 681-74, 1/8-INCH EXTRUSION

Run No.	4		5		6	
	Time, hr					
	236		267		315	
Analysis	Dry	Wet	Dry	Wet	Dry	Wet
Reactor Pressure, psig	375	375	375	375	380	380
Reactor Temp, °F	490	490	520	520	790	790
Top Zone No. 11	570	570	614	614	935	935
Bottom Zone No. 6	548	548	576	576	893	893
Feed Gas Flow Rate, SCF/hr	11.0569	11.1862	17.5725	17.8463	15.6650	15.9010
Feed H_2O Rate, lb-mol./hr	0.00036	0.00036	0.00073	0.00073	0.00064	0.00064
Feed Composition, mol %						
H_2	19.3	19.0	19.3	19.0	19.3	19.0
CH_4	68.7	67.9	68.7	67.6	68.7	67.7
CO	2.7	2.7	2.7	2.7	2.7	2.6
CO_2	2.6	2.6	2.6	2.6	2.6	2.6
N_2	2.4	2.4	2.4	2.4	2.4	2.4
C_2H_6	2.9	2.9	2.9	2.9	2.9	2.9
C_3H_8	1.28	1.2	1.28	1.2	1.28	1.2
He	0.07	0.07	0.07	0.08	0.07	0.07
H_2O	--	1.23	--	1.52	--	1.53
Total	99.95	100.00	99.95	100.00	99.95	100.00
Product Gas Flow Rate, SCF/hr	8.8399	9.0329	14.1761	14.5721	12.8935	13.4974
Product H_2O Rate, lb-mol./hr	0.00050	0.00050	0.00103	0.00103	0.00157	0.00157
Product Composition, mol %						
H_2	1.5	1.4	1.5	1.4	5.5	5.3
CH_4	87.6	85.7	87.2	84.8	87.6	83.7
CO	0.3	0.3	0.37	0.4	0.14	0.14
CO_2	3.5	3.4	3.9	3.8	2.4	2.3
N_2	2.0	2.1	2.5	2.4	2.7	2.6
C_2H_{6+}	3.7	3.6	3.0	2.9	1.2	1.1
C_3H_8	1.34	1.3	1.4	1.3	0.39	0.37
He	0.08	0.08	0.08	0.08	0.09	0.85
H_2O	--	2.12	--	2.92	--	3.64
Total	100.02	100.00	99.95	100.00	100.02	100.00
Component Consumed, lb-mol./hr (% change)						
CO	0.0007 (91%)	--	0.00109 (89%)	--	0.00105 (95%)	--
CO_2	nil --	--	nil --	--	0.000257 (24%)	--
H_2	0.0052 (94%)	--	0.00824 (94%)	--	0.006008 (77%)	--
C_2H_{6+}	nil --	--	nil --	--	0.00078 (66%)	--
C_3H_8	nil --	--	nil --	--	0.00039 (75%)	--
H_2O Produced, lb-mol./hr	0.00014	--	0.00030	--	0.00093	--
CH_4 Produced, lb-mol./hr	0.00038	--	0.00079	--	0.00138	--
Space Velocity, SCF/hr-cu ft	--	20,872	--	33,316	--	29,670

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Table 5-46. Part 3. LIFE STUDY DATA FOR CATALYST UC 684-74, 1/8-INCH EXTRUSION

Run No.	7		8		9	
	Time, hr					
	435		457		481	
Analysis	Dry	Wet	Dry	Wet	Dry	Wet
Reactor Pressure, psig	405	405	420	420	415	415
Reactor Temp, °F	890	890	610	610	610	610
Top Zone No. 11	1004	1004	786	786	717	717
Bottom Zone No. 6	977	977	768	768	670	670
Feed Gas Flow Rate, SCF/hr	16.3078	16.3556	5.5661	5.7202	0	0
Feed H_2O Rate, lb-mol./hr	0.00015	0.00015	0.00042	0.00042	--	--
Feed Composition, mol						
H_2	19.3	19.2	19.3	18.8	--	--
CH_4	68.7	68.5	68.7	66.8	--	--
CO	2.7	2.7	2.7	2.6	--	--
CO_2	2.6	2.6	2.6	2.5	--	--
N_2	2.4	2.4	2.4	2.4	--	--
C_2H_6	2.9	2.9	2.9	2.8	--	--
C_3H_8+	1.28	1.3	1.28	1.3	--	--
He	0.07	0.07	0.07	0.07	--	--
H_2O	--	0.33	--	2.73	--	--
Total	99.95	100.00	99.95	100.00	--	--
Product Gas Flow Rate, SCF/hr	13.8919	14.1214	4.5785	4.8073	--	--
Product H_2O Rate, lb-mol./hr	0.00060	0.00060	0.00060	0.00060	--	--
Product Composition, mol %						
H_2	9.0	8.9	6.8	6.5	--	--
CH_4	82.9	81.5	85.4	81.3	--	--
CO	0.9	0.9	0.15	0.15	--	--
CO_2	2.6	2.6	2.7	2.6	--	--
N_2	3.0	2.9	2.8	2.6	--	--
C_2H_6	1.0	1.0	1.6	1.5	--	--
C_3H_8+	0.49	0.5	0.45	0.4	--	--
He	0.08	0.08	0.08	0.08	--	--
H_2O	--	1.62	--	4.87	--	--
Total	99.97	100.00	99.98	100.00	--	--
Component Consumed, lb-mol./hr (% change)						
CO	0.00082 (72%)	--	0.00037 (95%)	--	--	--
CO_2	0.00016 (15%)	--	0.00005 (13%)	--	--	--
H_2	0.00492 (60%)	--	0.00198 (71%)	--	--	--
C_2H_6	0.00086 (71%)	--	0.00023 (55%)	--	--	--
C_3H_8+	0.00036 (67%)	--	0.00013 (72%)	--	--	--
H_2O Produced, lb-mol./hr	0.00046	--	0.00018	--	--	--
CH_4 Produced, lb-mol./hr	0.00081	--	0.00022	--	--	--
Space Velocity, SCF/hr-cu ft	--	30,518	--	10,673	--	--

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(Run 4 in Table 5-46). This test confirmed the previous finding, that the catalyst bed temperature should be kept above 550°F. All of the carbon monoxide in the feed was converted when the bed temperature passed 550°F and leveled at 573°F.

The breakthrough point was reached when the space velocity was increased to 33,000 standard cubic feet per hour per cubic foot (Run 5 in Table 5-46). While holding the space velocity at about 30,000 standard cubic feet per hour per cubic foot, the temperature of the reactor was increased to 935°F. Carbon monoxide conversion increased with increasing temperature. At 935°F, the product gas contained 0.14 percent carbon monoxide, or about 95% of the carbon monoxide in the feed was converted (Run 6 in Table 5-46). Carbon monoxide was completely converted again as soon as the space velocity was decreased to 10,000 standard cubic feet per hour per cubic foot.

The space velocity was increased to 30,000 standard cubic feet per hour per cubic foot, and the temperature was increased to 1004°F at the end of 435 hours. The steam content was decreased to 0.33 percent after 5 hours at these conditions. Carbon monoxide conversion decreased considerably, and the pressure dropped across the reactor bed increased (Run 7 in Table 5-46). The space velocity was decreased to about 10,000, the steam was increased to about 3 percent, and the temperature was decreased to 786°F. At the end of 457 hours, the conversion was still poor (Run 8 in Table 5-46), and the pressure drop across the bed continued to increase. The experiment was discontinued at the end of 481 hours.

It can be concluded that:

1) The UC 681-74 catalyst has good activity when compared with other catalysts.

2) It has high temperature resistance; however, steam must be present when the catalyst is subjected to temperatures higher than 1000°F to avoid carbon deposition. The activity of the catalyst may decrease once it has been at high temperature.

3) The lower temperature limit is 550°F at 600 psig or at higher pressures. (It is 500°F at 400 psig and 300°F at 0 psig). Deactivation may occur at lower than specified temperatures and the catalyst is not regenerable.

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