PILOT-PLANT STUDY OF AN ADIABATIC PARALLEL-PLATE METHANATION REACTOR

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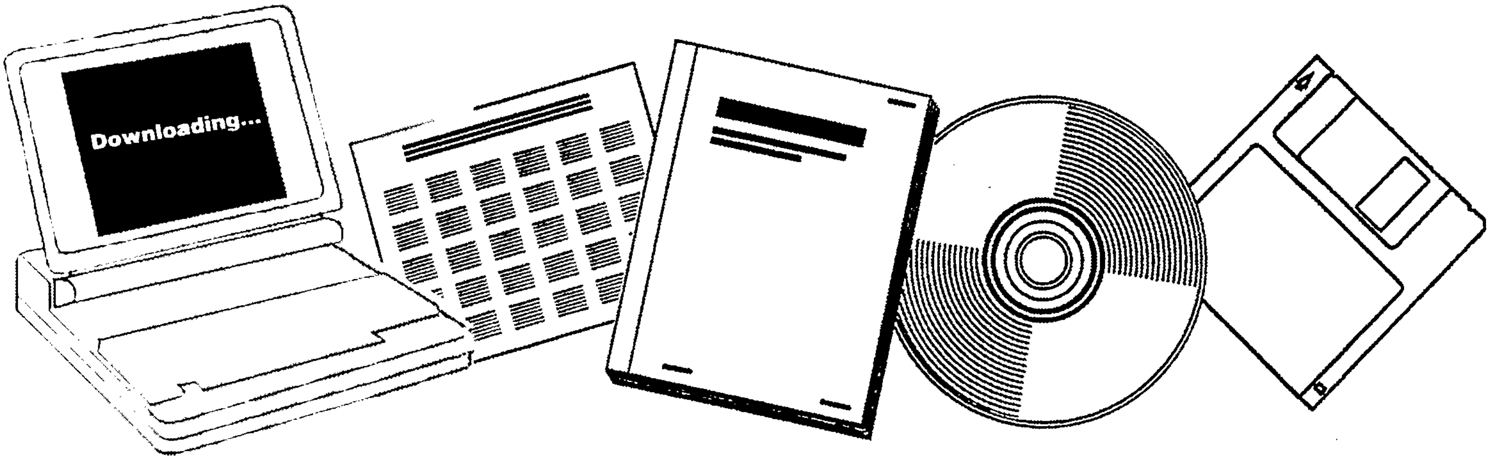

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by

W. P. Haynes, R. R. Schehl, J. K. Weber and A. J. Forney

Pittsburgh Energy Research Center

4800 Forbes Avenue, Pittsburgh, Pa. 15213

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ABSTRACT

Pilot plant data are presented from a 1291 hour test on an adiabatic catalytic methanation reactor employing recycled product gas for cooling. Topics discussed include conversion, product yields, catalyst properties and deactivation rates. A mathematical model postulating an irreversible Langmuir-Hinshelwood mode of deactivation is presented and applied.

INTRODUCTION

Virtually all of the processes currently under development for making synthetic natural gas from coal require a catalytic methanation step for upgrading the raw gas to a high Btu pipeline quality gas. The Energy Research and Development Administration, Pittsburgh Energy Research Center, is conducting bench-scale and pilot-plant scale studies of methanation with a variety of types of catalytic methanation reactors. This paper describes the pilot plant study of an adiabatic parallel plate methanator. This type of reactor is frequently referred to as a hot-gas-recycle reactor, as large quantities of partially cooled product gas are circulated through the catalyst bed in order to remove the heat of reaction. Previous experiments with the hot-gas-recycle reactor have been reported (1,2). The experiment discussed in this report was an attempt to compare the performance of a longer catalyst bed (8 ft.) with previous experiments using shorter beds (2 ft. and 5 ft.).

REACTOR DESCRIPTION

Experiment HGR-15 was performed in a pilot plant reactor constructed of type 304 stainless steel 3 inch schedule 40 pipe, 10 feet long, and flanged at each end. The catalyst bed consisted of grid assemblies of parallel type 304 stainless steel plates flame-sprayed with Raney nickel. Each grid assembly was 6 inches long, contained 15 plates, and was shaped to conform to the inside diameter of the reactor. As indicated in Figure 1, adjacent grid assemblies were rotated 90° with respect to each other. Prior to assembly, individual plates were sand-blasted on both sides with an iron-free grit and then flame-sprayed with a light coat of bonding material, about 0.007 inches thick. Subsequent to the bond coat, Raney nickel alloy powder (80-200 mesh) was flame sprayed onto the surface until the desired thickness was achieved (0.022 inches). The grids were assembled, placed in the reactor to form an 8 ft. bed, and then activated by passing a 2 wt. per cent solution of NaOH through the reactor until approximately 70 per cent of the aluminum in the Raney alloy was reacted. The extent of reaction was determined by measuring the quantity of hydrogen which evolves according to 3 moles of H_2 for every 2 moles of Al reacted. After activation, the catalyst was washed with water until the effluent water reached a pH of about 7.2. The reactor was maintained under hydrogen pressure until the temperature and pressure of the system was brought to synthesis conditions at which time the synthesis feed gas was gradually fed into the system to start the run. Pertinent catalyst bed data are given in Table 1.

Figure 2 is a simplified flowsheet of the hot-gas-recycle pilot plant. The primary reactor consisting of the parallel plate grid assemblies is only considered in this report. The second stage reactor, an adiabatic reactor charged with a precipitated nickel catalyst, was operated only during the later periods of the run. Additional heat exchangers, not illustrated, were used in the pilot plant to compensate for system heat losses, to achieve a measure of heat recuperation, and to control the gas temperature into the hot gas compressor and into the primary reactor. Cooling of the catalyst bed is achieved by direct transfer of the heat of reaction to the slightly cooler gas stream flowing through the bed. The hot recycle stream may be cooled either directly without condensation or by cooling a portion of the recycled product gas sufficiently to condense out the water vapor and then returning the resulting cold recycle gas along with the hot recycle gas. After a final heat exchange, the mixture of the cooled recycle gas and the fresh feed gas constitute a feed to the hot gas recycle reactor at a controlled temperature that may be 50-150°C lower than the reactor outlet temperature, depending upon the total amount of gas recycled and the extent of heat exchange.

OPERATING PROCEDURES AND RESULTS

The operating conditions for run HGR-15 were similar to those for run HGR-14 (1) (HGR-14 consisted of a 2 ft. bed of catalytic grids).

with the exceptions that the fresh feed space velocity remained constant at 2000hr^{-1} (at the very end of the experiment the space velocity was decreased to 1500 and then to 1000hr^{-1} for a few periods) and the cold gas recycle (CGR) to fresh feed ratio was maintained constant at 3. Space velocity calculations were based on an empty reactor volume. The operating parameters studied and the product gas characteristics are presented in Figures 3 and 4 respectively.

Performance of run HGR-15 compared unfavorably with run HGR-14 as the catalyst life was shorter (1291 hours compared to 2307 hours for HGR-14) and the initial product CO concentration was higher (0.09 per cent compared to 0.01 per cent).Five shutdowns occurred during the run at 22, 109, 207, 494 and 811 hours on stream due to compressor and heat exchanger repair. Before cooling the catalyst to take it out of service, the reactor was purged with hydrogen. It was kept in a hydrogen atmosphere during cooling, depressurizing and stand-by condition. At 955 hours the temperature rise across the reactor was increased to 125°C. The CO conversion temporarily increased during the first 48 hours but then continued to decrease at the same rate as the T=100°C operating condition. At 1150 hours T=100°C was reinstated, resulting in a further decrease in conversion. Since the overall catalyst activity was already declining rapidly, the effect of increased temperature drop is difficult to assess. The product CO concentration at the end of operation at 2000 hr^{-1} fresh feed gas space velocity was 1.10 volume per cent. The total CH_4 production per lb. of catalyst was 15.0 MSCF/lb.

Selected tabulated periods in run HGR-15 are presented in Table 2.

Period 2	represents performance at 2000hr^{-1} fresh feed gas space velocity and 3:1 cold recycle when the catalyst is fresh.
Period 33 and 34	provides a comparison of prior to and immediately following a change in catalyst temperature spread to 125°C T.
Period 41 and 42	represents the conclusion of 125°C T and the beginning of 100°C T operating conditions
Period 44	represents operation at 1500 hr^{-1} fresh feed gas space velocity at 3:1 CGR and 7:1 HGR ratios.
Period 45	represents operation at 1000 hr^{-1} fresh feed gas space velocity at 3:1 CGR and 7:1 HGR ratios.

The analysis of catalyst plate scrapings are shown in Table 3. It is apparent from these analysis that sulfur poisoning and fouling due to carbon deposition during run HGR-15 increased over that during HGR-14. Several items concerning these data should be emphasized.

1. Increased sulfur poisoning in HGR-15 existed; 0.26% sulfur compared to 0.16% sulfur in HGR-14 on the reactor inlet plates.
2. Increased carbon deposition in HGR-15; 4.5% compared to 3.25% on same inlet plates and 0.9% to 0.61% on the exit plates.
3. A consistent decreased amount of nickel in the HGR-15 samples, i.e. an average of 57.33% on the HGR-15 plates compared to an average of 78.05% in HGR-14. This would indicate incomplete leaching.
4. X-ray analysis of the spent catalyst revealed metallic nickel and nickel carbide, Ni_3C, in the catalyst near the gas inlet and only metallic nickel near the gas outlet, indicating that carbiding

occurred during both runs.

5. An increased percentage of nickel on the bottom plate of HGR-15; 64.4% compared to 52.2% on top plate, indicating non-uniform leaching.

6. Plate thickness of the top and bottom assemblies were measured after removal of the activated portion of the catalyst. The average plate thickness of the bottom plates was 0.078" and the top plates 0.091". This is further indication of non-uniform leaching occurring more extensively at the reactor bottom. Furthermore, the thickness of the middle portion of the plates from both sets of assemblies was less than the end thicknesses. There is no immediate explanation for this difference. Average plate thickness data are represented in Table 4. Certain runs subsequent to HGR-15 have utilized recirculation of the caustic solution in order to achieve more uniform leaching of the Raney nickel catalyst. Results of this technique are not yet available.

The spent catalyst was examined for surface area and pore volume characteristics. These data are tabulated in Table 5. The higher surface area at the inlet of run HGR-15 is very likely a result of the larger percentage of carbon deposits on these plates. Metal surface area measurements were not performed on the spent catalyst samples. Measurements made on samples from previous runs indicated that the nickel metal sites were fewer at the reactor inlet even though the BET surface area was greater at the inlet than at the exit.

Table 6 lists superficial deactivation rates for the catalyst bed in run HGR-15. The superficial deactivation is given by the change in product CO percent per MSCF of CH_4 produced per lb. of catalyst in the bed. It will be noticed that there is a general increase in superficial deactivation rate with time on stream. This is precisely the behavior a "zonal burn-out" type catalyst bed deactivation would exhibit.

APPLICATION OF A MATHEMATICAL MODEL TO RUN HGR-15

A recent publication (3) presented a mathematical model along with some applications of a tube-wall methanation reactor to be utilized in the ERDA Synthane process. This model made no provisions for deactivation of the catalyst. The model has been improved by taking into account catalyst deactivation with increasing time on stream and to extend the model to applications in hot-gas-recycle methanation.

The mechanism responsible for deactivation of flame sprayed Raney nickel catalyst is not thoroughly understood at the present time. It is possible that deactivation is caused by several processes acting simultaneously, such as sintering, poisoning by trace amounts of sulfur in the feed stream, and trace amounts of iron carbonyl depositing in an active site which subsequently acts as a center for carbon deposition. The model presupposes the following:

1. The catalyst is poisoned via some mechanism independent of that of the main reaction, that is, the feed contains a trace amount of some unspecified poison. The reactions may be written

$$CO + 3H_2 \overset{k}{\rightleftharpoons} CH_4 + H_2O \text{ (main reaction, fast)}$$

$$P \xrightarrow{k_P} W \qquad \text{(poisoning reaction, slow).}$$

It is assumed that the poison reaction is much slower than the main reaction.

Consequently, the main reaction may be assumed to approach a steady state behavior over a short period of time. This assumption has the effect of decoupling the equations associated with the main reaction model from those associated with the poisoning model.

2. Since there is little experimental evidence with regard to the poisoning mechanism, an irreversible Langmuir-Hinshelwood type of expression for the rate of formation of adsorbed poison is assumed.

The kinetic rate expression for the conversion of CO to CH_4 was taken to be that proposed by A. L. Lee (4,5) which provides a reasonable fit to data reported by IGT. Lee's rate expression developed from supported nickel catalysts is of the form,

$$r_L = \frac{k_1\, e^{-E/RT'}\, P_{CO} P_{H_2}^{0.5}}{1 + k_2 P_{H_2} + k_3 P_{CH_4}} \quad . \tag{1}$$

This rate equation was simplified, to a certain extent, in the present analysis to the following form;

$$-r = k\, e^{-E/RT} \tilde{C}_{CO} C_{H_2}^{0.5} \quad . \tag{2}$$

Carbon monoxide is the limiting reactant in the hot-gas-recycle methanator. Inlet H_2/CO ratios are typically on the order of four to five while the stoichiometric ratio for the methanation reaction is three. This coupled with the higher diffusivity of hydrogen (approximately three times that of CO) leads to the assumption that the H_2 concentration at the catalyst surface is the same as the bulk hydrogen concentration. In our application, the denominator of equation 1 will change only a few per cent from the inlet to the exit of the catalyst bed while the numerator changes roughly two orders of magnitude. Hence, little error is introduced through simplifying equation 1 to equation 2.

At steady state conditions there is no net change in reactant concentrations at the catalyst surface, thus, the rate of reaction must equal the rate at which CO diffuses to the catalyst surface. The mass transfer rate is given by

$$-r = k_c(C_{CO}-\tilde{C}_{CO}) \ , \tag{3}$$

where k_c is the film mass transfer coefficient. The mass transfer coefficient is calculated, for a given Reynold's number, from the standard j-factor correlation (6,7).

Equations 2 and 3 may easily be solved for $\tilde{C}_{co}$ giving

$$\tilde{C}_{CO} = C_{CO}k_c/(k_c + k\ e^{-E/RT}\ C_{H_2}^{0.5}) \ .$$

Substitution of the expression for $\tilde{C}_{co}$ back into either equation 2 or 3 yields the global reaction rate expressions in terms of the bulk concentrations;

$$-r = k_c\ C_{CO}\left[1 - 1/(1 + \frac{k}{k_c}\ e^{-E/RT}\ C_{H_2}^{0.5})\right] . \tag{4}$$

Since the reactor is operating adiabatically, there could be an appreciable temperature dependence in the global rate expression which is accounted for through the Arrhenius type expression. Knowledge of the catalyst temperature is required to evaluate this expression, hence, we write:

$$r\mathcal{H} = h\ (T-T') \tag{5}$$

and

$$r\mathcal{H} = C_p\ M\ \frac{\partial T'}{\partial A} \ . \tag{6}$$

h is the film heat transfer coefficient and is evaluated in a manner similar to that of k_c. Equation 6 is used to calculate the gas temperature as a function of distance through the reactor and, given T', the catalyst temperature may be estimated from equation 5.

The poisoning mechanism assumed in this paper is that of the irreversible adsorption of compounds other than the principle reactants and products on the catalytically active sites. This is commonly referred to as Type I, or independent poisoning. In the absence of any experimental evidence to the contrary, it is reasonable to assume an irreversible Langmuir-Hinshelwood type of expression for the rate of formation of adsorbed poison;

$$r_p = k_p\, C_D\, (1 - \sigma/\sigma_T). \qquad (7)$$

In dimensionless form, equation 7 and a differential mass balance of the poison species across an element of the catalyst surface become, respectively,

$$\frac{\partial\psi}{\partial\Theta} = \phi(1-\psi) \qquad (8)$$

and

$$\frac{\partial\phi}{\partial\alpha} = -N_D\, \phi(1-\psi). \qquad (9)$$

Equations 8 and 9 must be solved simultaneously for ψ and ϕ as functions of Θ and α. If the catalyst bed is initially free of adsorbed poison and the concentration of poison precurser in the feed remains constant with time, then the following boundary conditions are applicable:

$$\psi(0,\alpha) = 0$$
$$\phi(\Theta,0) = 1. \qquad (10)$$

The analytical solution of this system is of the form,

$$\psi(\Theta,\alpha) = (1-e^{-\Theta})/(1 + e^{-\Theta}(e^{N_D\alpha}-1))$$

and the function $\psi(\Theta,\alpha)$ may be directly related to the catalyst activity at any point (Θ,α) as follows:

$$k = k_{initial}\ (1-\psi)$$

provided that the initial catalyst activity is uniform over the entire catalyst bed.

$\psi(\Theta,\alpha)$ contains two parameters which must be determined from experiment as there is insufficient independent data to predict them _a priori_. Let these parameters be called p_1 and p_2 and be defined by

$$p_1 = \Theta/t = k_p C_D^\circ/\sigma_T$$

$$p_2 = N_D\alpha/A = k_p/V\ .$$

The ratio p_1/p_2 is a measure of the 'velocity' of the deactivation front as it traverses the catalyst bed while p_2 is proportional to the slope of the activity profile at its point of inflection.

The model outlined above has essentially three parameters which must be obtained from experimental data; $k_{initial}$, p_1 and p_2. Other parameters such as physical properties of the gas, transfer coefficients, activation energy and heat of reaction may be estimated from data published in the literature. Ideally, $k_{initial}$ can be determined from data obtained early in the run when deactivation of the catalyst bed is negligible. Similarly, the ratio p_1/p_2 may be estimated by measuring the 'velocity' of the global reaction zone as it moves down the reactor. This leaves only p_1 or p_2 to be fitted to experimental temperature profile data.

Unfortunately, there were numerous unscheduled shut-downs during run HGR-15. During a shut-down, the catalyst is maintained in a 50 to 100 psig hydrogen environment which induces a partial recovery of the catalyst activity. This adds another dimension, not easily accountable, to the poisoning model. Another complication was the apparent faster deactivation rate during the first 200 hours of the run. At 207 hours on stream the hot-gas-recycle compressor was overhauled. Prior to this time it is possible that the catalyst was exposed to higher concentrations of oil vapor from this compressor.

A fit of the model to experimental data, using an activation energy of 1.25×10^4 Btu/lb mole (5) yielded the values $k \simeq 1.1 \times 10^6\ \mathrm{ft}^{5/2}/\mathrm{hr}\text{-}\mathrm{lb\ mol.}^{1/2}$, $p_1 \simeq 0.0114$ (0 - 207 hours on stream), $p_1 \simeq 0.00625\mathrm{hr}^{-1}$ (times succeeding 207 hours) and $p_2 \simeq 0.2\mathrm{ft}^{-2}$. Typical comparisons of the model predictions with experimental data are shown in Figures 5 and 6. Figure 5 illustrates the fit of calculated gas temperatures profiles to experimentally measured temperatures for several different times on stream. Figure 6 compares the calculated and observed CO concentrations as functions of distance through the reactor and time on stream. Figure 7 demonstrates the simulation of product CO concentrations for the first 1150 hours. Agreement between model and experiment is seen to be remarkably good. At 955 hours the temperature rise through the catalyst bed was increased to 125°C. Figure 7 indicates that a comparison of calculated catalyst temperature with experimental and calculated gas temperatures at 347 hours on stream. The maximum temperature difference between catalyst and gas is approximately 20°C. The relative catalyst activity is also plotted to indicate the extent of catalyst deactivation at this time on stream.

Because of the increased number of shutdowns and unsatisfactory leaching, an equitable comparison of runs HGR-15 and HGR-14 cannot be made. Another significant difference between the runs was flow condition of the gas stream. HGR-14 was operated in laminar flow (N_{Re}= 1200-1800) whereas HGR-15 was turbulent (N_{Re}= 4000-5000). Additional experiments should be performed to test the capability of the model to predict reactor performance under dimensional scale-up and different operating conditions such as total system pressure and space velocity.

ACKNOWLEDGEMENTS

We acknowledge with thanks J. J. Elliott and H. Pennline for their work in supervising the operation of the pilot plant methanation reactors.

NOMENCLATURE

A = superficial catalyst surface area (ft^2)

A_o = total superficial catalyst surface area (ft^2)

C = concentration in bulk gas (lb-mol./ft^3)

$\tilde{C}$ = concentration at catalyst surface (lb-mol./ft^3)

C_D = poison concentration in gas (lb-mol./ft^3)

C_D^o = poison concentration in feed (lb-mol./ft^3)

C_p = specific heat of gas (Btu/lb. mol. - °F)

E = activation energy (Btu/lb-mol.)

[illegible] = heat of reaction (Btu/lb. mol.)

h = heat transfer coefficient (Btu/hr-ft^2-°F)

k, k_1 = rate constants

k_2, k_3 = equilibrium constants

k_p = poisoning rate constant

k_c = mass transfer coefficient (lb-mol./hr-ft^2- concentration difference)

M = gas molar flow rate (lb mol./hr)

$N = A_o k_p / V$, dimensionless constant

P = partial pressure (psi)

R = gas constant (Btu/lb-mol.-°R)

r = rate of CO conversion (lb-mol./hr-ft^2 catalyst)

r_1 = rate of methane formation (lb-mol./hr-g catalyst)

r_p = rate of formation of adsorbed poison (lb mol./hr-ft^2 catalyst)

t = real time (hours)

T = catalyst temperature (°R)

T' = gas temperature (°R)

V = volumetric flow rate of gas through reactor (ft^3/hr)

α = $A/_{A_o}$, dimensionless superficial catalyst surface area

θ = $k_p C_D^\circ\ t/\ {}_T$, dimensionless time

σ = poison concentration on catalyst surface (lb-mol./ft^2)

σ_T = value of σ corresponding to complete deactivation (lb. mol./ft^2)

ϕ = C_D/C_D°, dimensionless concentration

ψ = σ/σ_T dimensionless concentration

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TABLES

ILLUSTRATIONS

Table 1. - Catalyst Bed Data for HGR-15

Type catalyst	Flame-sprayed Raney nickel
Wt pct nickel	42[a]
Pct activated	70[b]
Plate thickness, in.	0.048
Space between bare plates, in.	0.135
Av. bond coat thickness, in.	0.007
Av. catalyst thickness, in.	0.022
Bed diameter x length, in.	3.07 x 96
Bed volume, ft^3	0.41
Weight of unactivated catalyst, lb.	15.47
Superficial area of catalyst, ft^2	45.64
Void fraction	0.500

[a] Before leaching

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

Table 2. - Experiment HGR 15-Selected Test Data

Period Number		2	33	34	41	42	44	45
Hours on stream		91	955	979	1147	1171	1219	1243
Fresh Gas:								
Rate..............	scfh	810	821	820	822	823	617	411
H_2	vol pct	75.1	75.3	74.6	75.1	75.3	74.7	75.5
CO	vol pct	24.5	23.8	24.5	24.5	24.2	24.2	23.7
CO_2...............	vol pct	0.1	0.1	0.1	0.2	0.1	0.2	0.2
N_2	vol pct	0.3	0.7	0.7	0.2	0.3	0.8	0.5
CH_4	vol pct	0	0.1	0.1	0	0.1	0.1	0.1
H_2/CO		3.1	3.2	3.0	3.1	3.1	3.1	3.2
Exposure vel......scfh/ft^2		17.8	18.0	18.0	18.0	18.0	13.5	9.0
Space vel............	hr^{-1}	1990	1986	2013	2015	2017	1512	1008
Mixed feed gas (wet):								
Rate	scfh	12000	9750	7600	8700	10150	6780	4470
H_2	vol pct	8.5	13.5	14.0	13.4	13.7	13.0	12.5
CO	vol pct	1.7	2.5	3.0	3.0	2.7	2.8	2.4
CO_2...............	vol pct	1.0	0.5	0.5	0.7	0.7	0.6	0.5
N_2	vol pct	3.5	0.9	0.8	1.1	0.8	0.9	0.3
CH_4...............	vol pct	79.2	78.0	77.7	77.6	77.5	78.4	79.9
H_2O	vol pct	6.1	4.6	4.0	4.2	4.6	4.3	4.4
H_2/CO.....................		5.1	5.4	4.7	4.5	4.9	4.6	5.1
Inlet superficial vel..f/s		6.4	5.2	4.0	4.6	5.4	3.6	2.4
Inlet Reynolds No.........		5660	4400	3440	3920	4580	3060	2040
Exposure vel.......scfh/ft^2		263	214	166	190	222	149	98
Space vel.............	hr^{-1}	29400	23900	18600	21250	24900	16620	10950
Vol. total recycle/vol.fresh gas		14.0	11.1	8.5	9.8	11.6	10.2	10.1
Vol. cold recycle/vol.fresh gas		2.5	3.0	3.0	3.0	3.0	3.0	3.1

continued:

Table 2. - Experiment HGR-15 - Selected Test Data

Period Number	2	33	34	41	42	44	45
Temperatures:							
Gas Inlet ....°C	302	301	302	301	300	300	302
Maximum catalyst ....°C	395	400	423	425	400	399	400
Pressure ....psig	300	300	300	300	300	300	300
Product gas:							
Rate ....scfh	206.0	212.3	208.6	210.9	211.7	156.4	103.8
H_2..............vol pct	4.0	8.2	6.9	7.2	8.6	7.1	6.4
CO..............vol pct	.03	0.6	0.4	0.7	0.9	0.7	0.3
CO_2.............vol pct	1.17	0.5	0.6	0.8	0.8	0.6	0.5
N_2 ....vol pct	3.9	1.0	0.9	1.2	0.9	1.0	0.3
CH_4.............vol pct	90.7	89.5	91.0	89.9	88.6	90.4	92.3
H_2O ....vol pct	0.2	0.2	0.2	0.2	0.2	0.2	0.2
H_2/CO..................	133.0	13.7	16.9	9.6	9.3	10.4	21.4
Conversion:							
H_2........pct fresh feed	98.7	97.6	98.0	98.0	97.6	98.3	98.8
CO........pct fresh feed	100	99.5	99.7	99.4	99.2	99.5	99.8
(H_2+CO)...pct fresh feed	99.0	98.1	98.4	98.3	97.9	98.6	99.0
H_2........pct mixed feed	58.4	45.6	56.3	52.0	43.4	51.2	54.4
CO........pct mixed feed	98.4	78.8	88.0	77.6	70.0	78.3	89.1
(H_2+CO)...pct mixed feed	65.0	50.8	61.8	56.7	47.9	56.0	60.1
Usage ratio................	3.0	3.1	3.0	3.0	3.0	3.0	3.1
Heating value ......BTU/scf	934	937	947	937	931	943	959
Carbon recovery.........pct	95.0	100	96.7	97.0	97.3	96.0	96.5

Table 3. - Properties of Spent Raney Nickel Catalyst

		Run 14*		Run 15		
		Reactor Inlet (Top)	Reactor Outlet (Bottom)	Reactor Inlet (Top)	Reactor (Middle)	Reactor Outlet (Bottom)
X-Ray analysis		Ni,Ni_3C	Ni	Ni,Ni_3C	Ni,Ni_3C	Ni
Chemical analysis, per cent						
	Ni	78.45	77.65	52.60	54.70	64.70
	Al	8.41	9.43	-	-	-
	C	3.25	0.61	4.50	3.80	0.90
	Fe	0.88	0.96	0.24	0.25	0.27
	Na	-	-	0.16	0.12	0.12
	S	0.16	0.07	0.26	0.16	0.003

* average of two samples

Table 4. - Average Plate Thickness Data of HGR-15 After Removal of Spent Catalyst

Top Plate Assemblies			Bottom Plate Assemblies		
End	Middle	End	End	Middle	End
0.091"	0.085"	0.098"	0.081"	0.073"	0.081"

Table 5. - Surface Areas, Pore Volumes, and Pore Radii of Spent Raney Nickel Catalyst

	HGR-14*		HGR-15	
Plates	Inlet	Outlet	Inlet	Outlet
Surface Area, m^2/gm	22.65	29.63	45.10	29.04
Pore Vol., cm^3/gm	0.055	0.089	0.128	0.094
Average Pore Radius, Å	48.77	60.02	56.67	65.06
Percent pore volume with the following radii:				
<30Å	16.27	9.70	13.46	9.59
30-40Å	16.72	9.99	10.16	8.84
40-50Å	13.34	9.71	9.60	5.53
50-60Å	10.00	8.20	9.78	9.12
>60Å	43.68	62.41	57.00	66.92
Percent total surface area with the following radii:				
<30Å	32.03	26.31	30.38	24.13
30-40Å	23.46	17.46	16.66	16.63
40-50Å	14.57	13.17	12.09	7.38
50-60Å	8.90	9.02	10.10	10.80
>60Å	21.05	34.05	30.77	40.56

* average of two samples

TABLE 6. - Superficial Catalyst Deactivation Rate Data.

Nominal Fresh Feed Space Velocity, hrs^{-1}	Stream from	Period to	hrs	Catalyst Deactivation Rate, percent/MSCF/lb-catalyst
2000	0	207	(to 3rd shutdown)	3.7×10^{-3}
2000	207	494	(to 4th ")	21.9×10^{-3}
2000	494	931	(to T=125° C operating conditions)	87.7×10^{-3}
2000	1003	1150	(T=125°C operating conditions)	147.5×10^{-3}
2000	1150	1196	(return to T=100° C operation)	569.1×10^{-3}

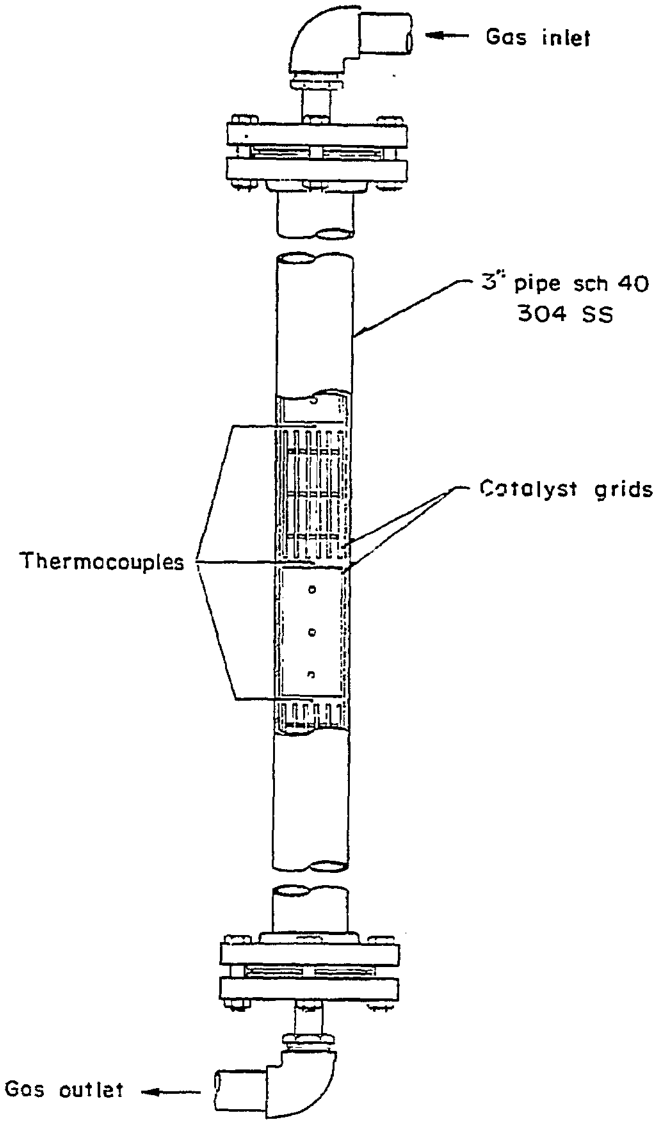

Figure 1. Hot-gas-recycle methanation reactor.

L-13468

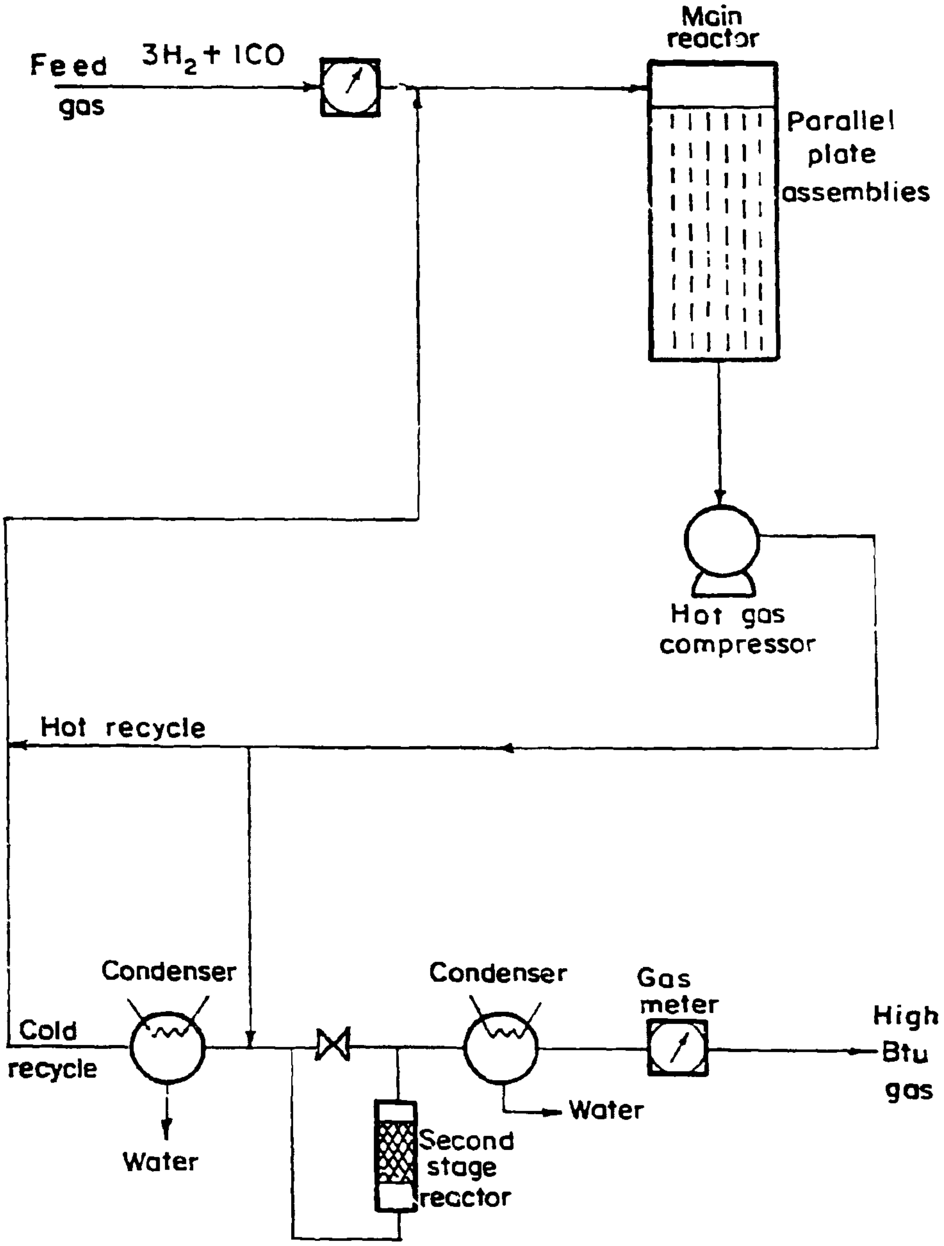

Figure 2. Flowsheet of hot-gas-recycle process.

L-13681

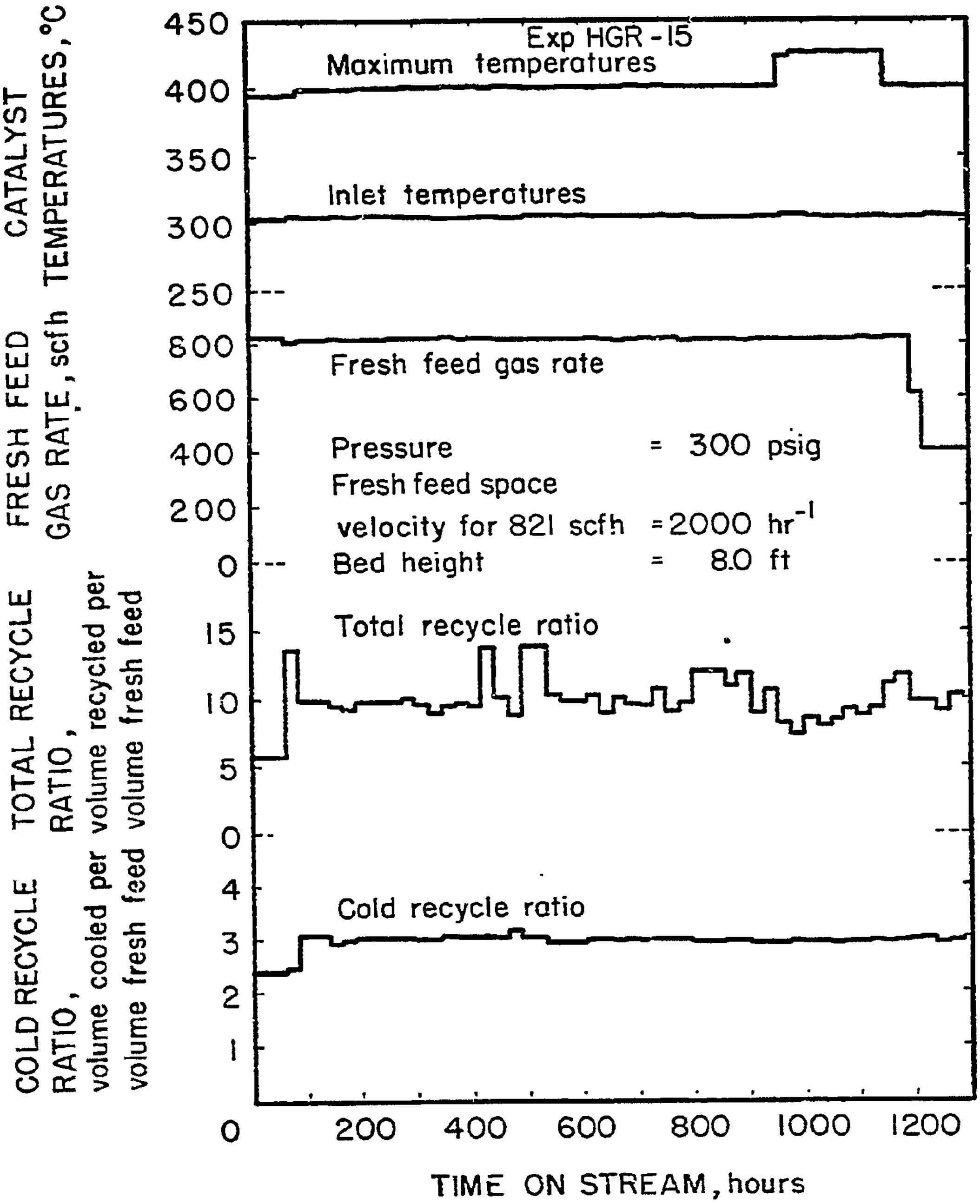

Figure 3. Reactor conditions

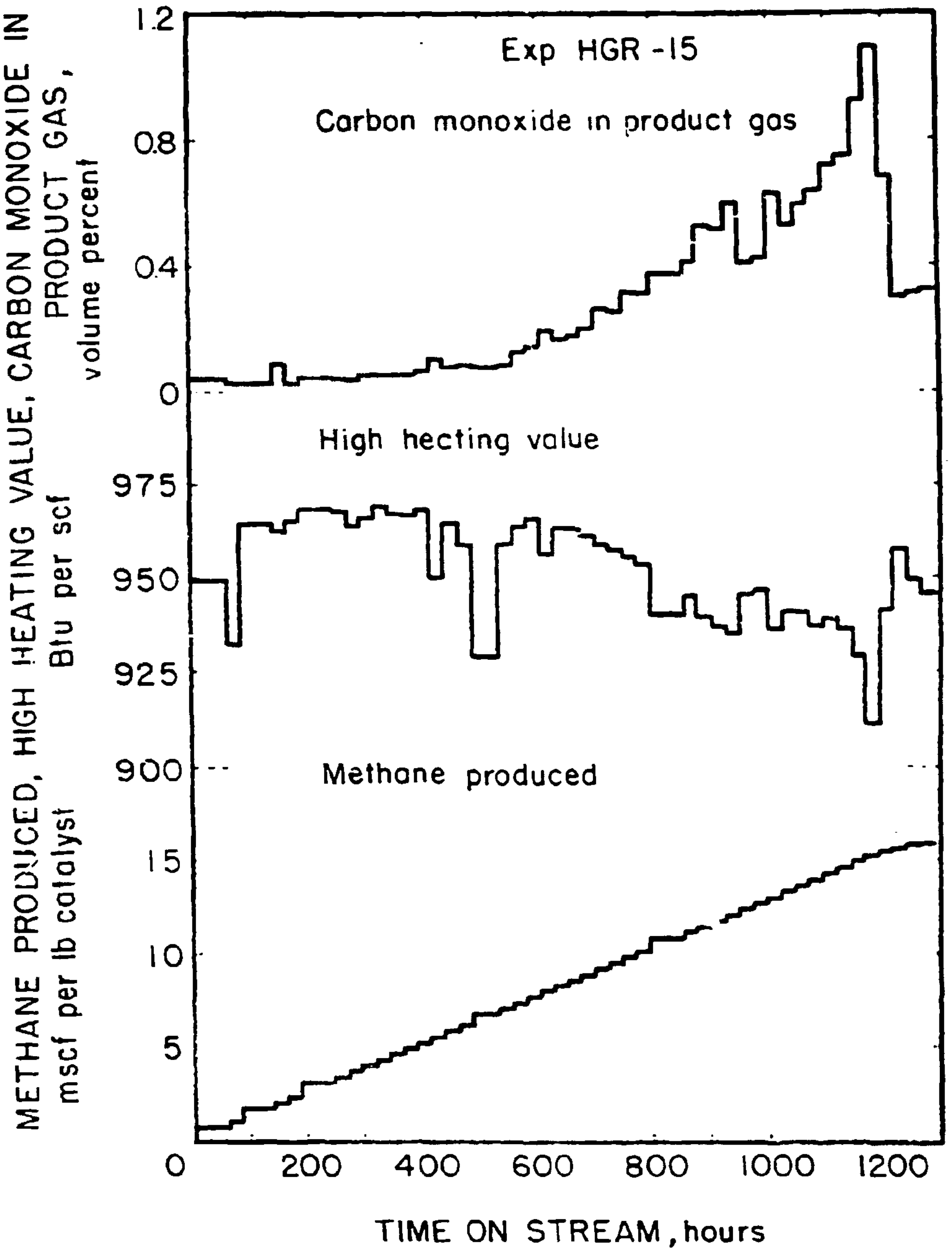

Figure 4. Product gas characteristics.

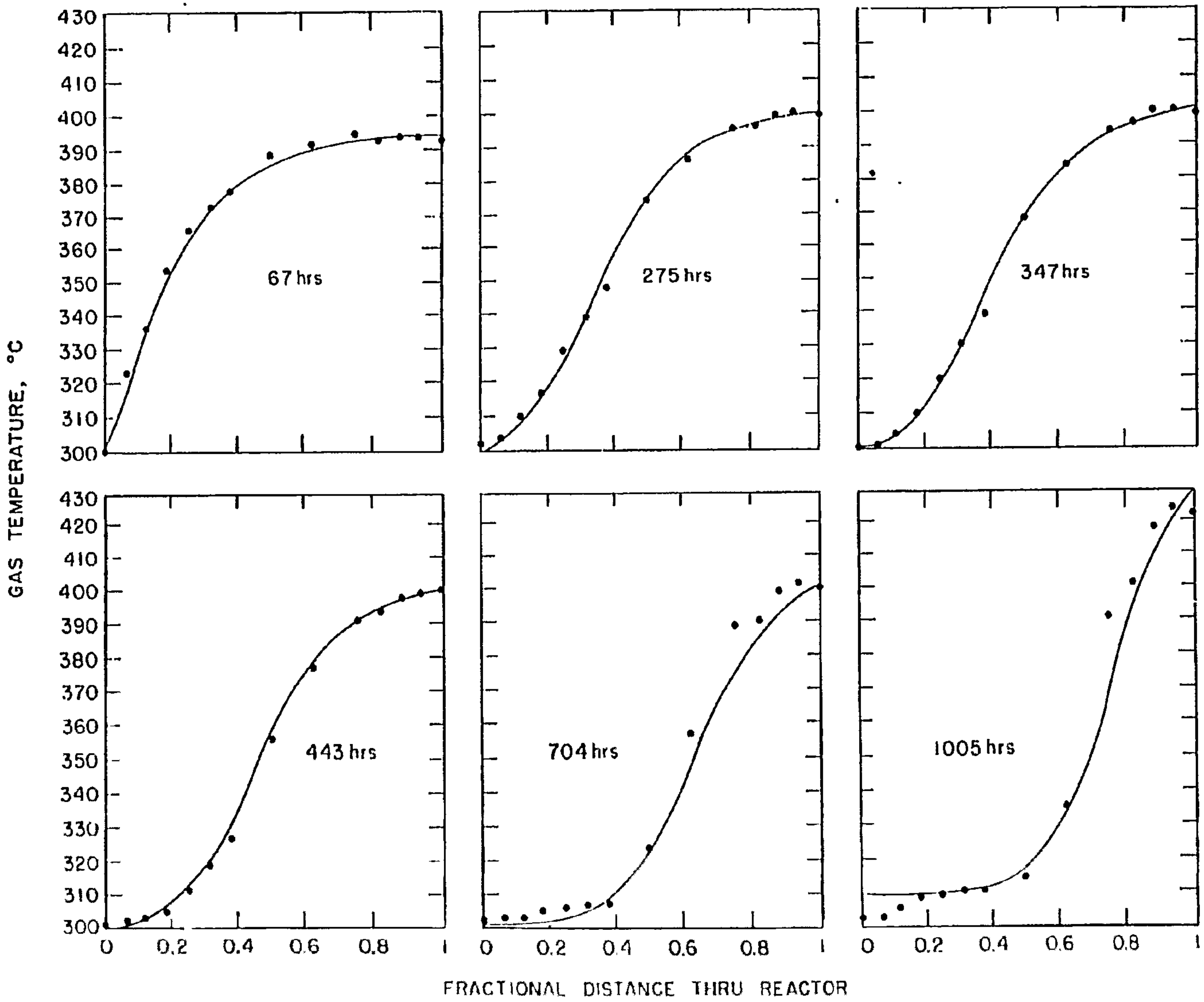

Figure 5. Gas temperature profiles for different times on stream model (———) experimental (●).

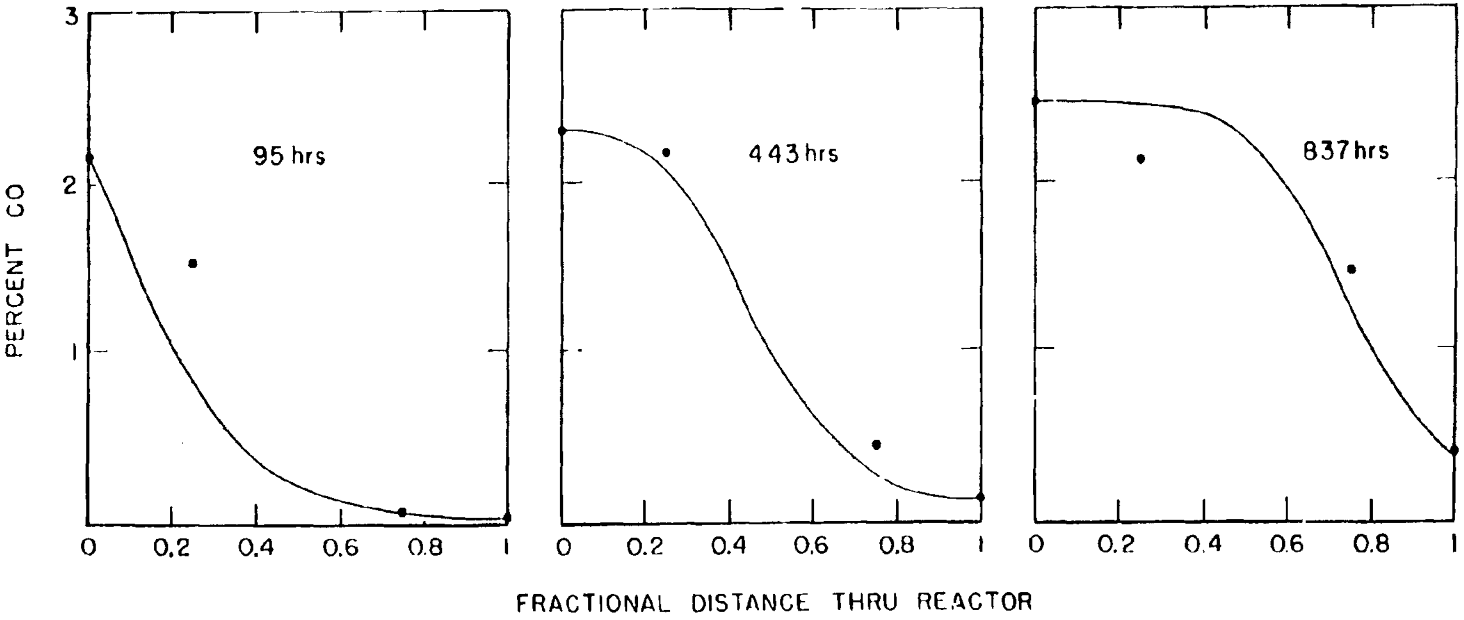

Figure 6. CO concentration profiles for different times on stream, model (———) experimental (●).

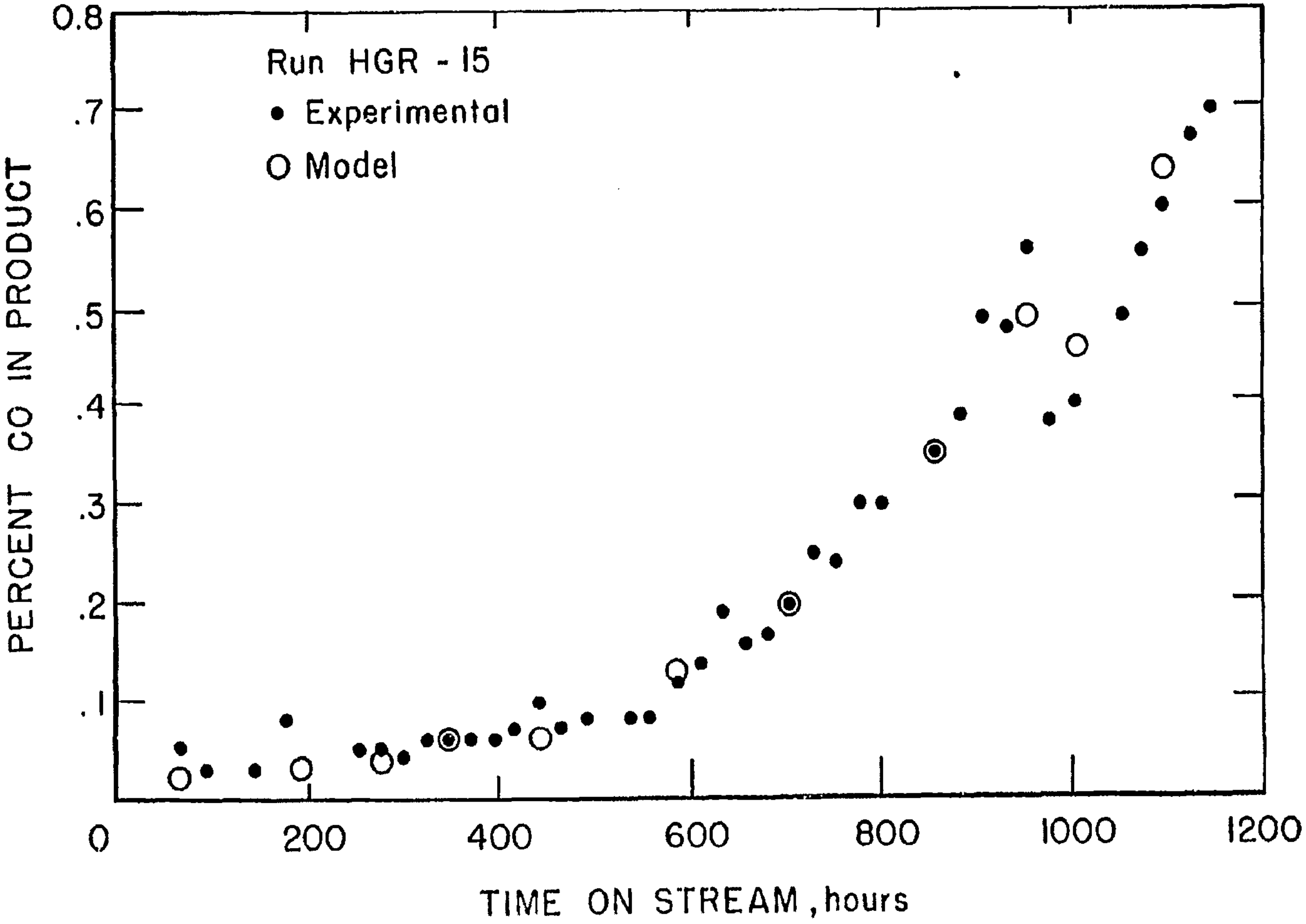

Figure 7. CO concentration in the product stream as a function of time on stream.

L-14232

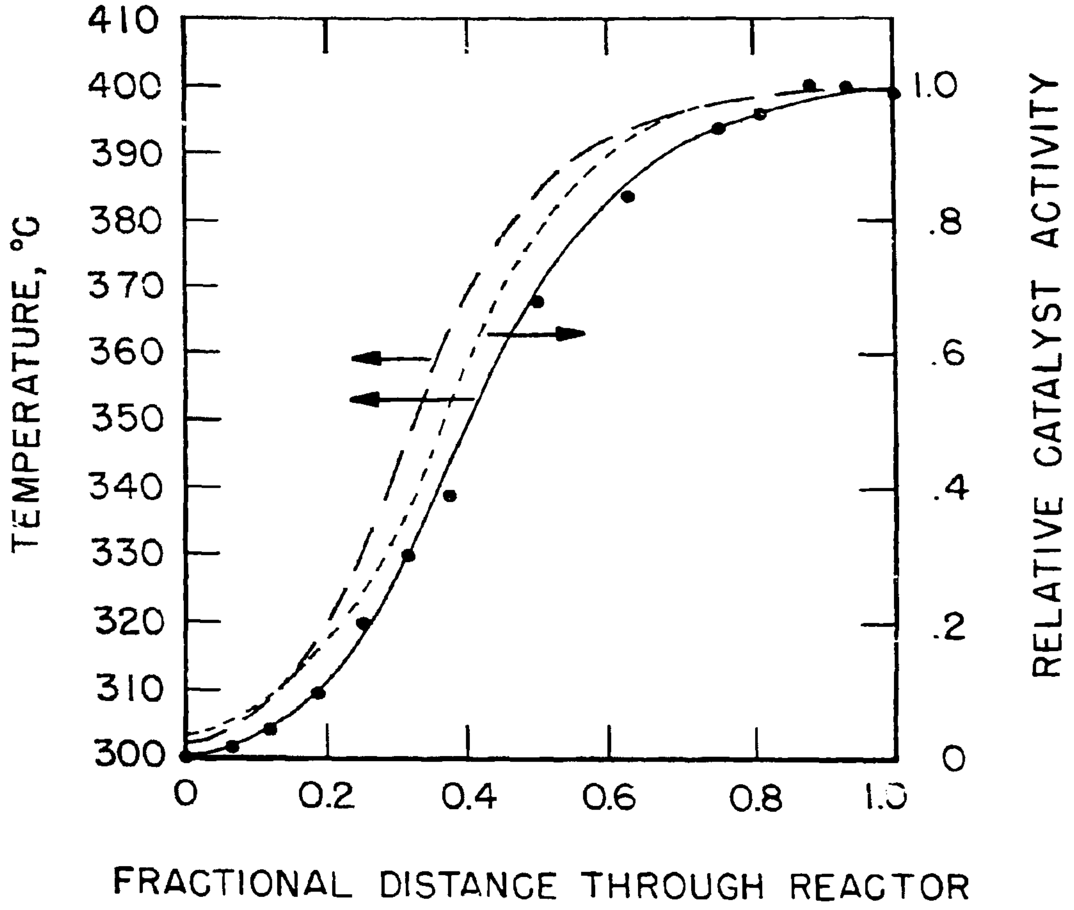

Figure 8. Comparison of calculated catalyst temperature (— —) with experimental (●) and calculated (———) gas temperatures at 347 hours on stream. Relative catalyst activity (-----).

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