IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

A. Bench Scale Work

1. Calsicat Ni-230S/Witco 40 Mineral Oil Reaction Rate Studies

During July, 1975 a process variable scan was initiated for the combined shift/methanation reaction using feed gases with various H_2/CO ratios with the Calsicat Ni-230S 1/16" spheres/Witco 40 mineral oil system. The catalyst activity was determined first with a $3H_2/1CO$ feed gas at 500 psig and 600^oF. For the above conditions, the initial value of the rate constant, $\frac{k\ (3/R)}{K_H\ M/\rho_L}$, was 2.61 x 10^{-6} gm mole/gm cat-atm-sec at 600^oF. During the first three hours on-stream, the catalyst activity declined to an equilibrium value of 1.16 x 10^{-6}, a 44 percent loss in activity which was typical for this catalyst formulation. After the catalyst had equilibrated in activity, the temperature was raised to 650^oF and the rate constant was determined to be 2.1 x 10^{-6}. Table IV-A-1a summarizes the data obtained with this system.

The feed gas composition was then switched to a $2H_2/CO$ ratio and data points were taken at 900 psig and 650^oF. The initial value of the rate constant for this feed composition was 1.75 x 10^{-6}, somewhat lower than obtained with the $3H_2/1CO$ feed gas. Subsequent runs showed daily sharp declines in activity. It was eventually determined that the cause of this deactivation was due to repeated depressurization (through leakage) of the reactor system while on standby overnight. The unit was shut down and the piping completely overhauled in order to re-establish a leak-free system.

Following this a new batch of Calsicat Ni-230S catalyst charge was loaded and reduced. The initial data points focussed on establishing

Table IV-A-1a

Process Variable Scan: 75% H_2 - 25% CO
Calsicat Ni-230S (1/16" spheres)[1]/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	VHSV Hr^{-1}	CO Conversion %	$\frac{k\,(R/3)}{K_H\,(M/\rho_L)} \times 10^6$
1A	600	510	6065	88.6	2.61
1B	600	510	3570	96.05	2.45
2A	594	510	6200	84.77	2.31
2B	593	510	5280	89.45	2.35
2C	586	510	2840	97.36	2.04
3A	625	520	4013	97.20	2.85
3B	653	520	4820	92.34	2.45
4A	650	500	6270	80.61	2.12
4B	606	500	3990	79.94	1.29
4C	606	500	6445	66.09	1.44
5A	600	500	7120	61.04	1.36
5B	599	500	4405	72.10	1.14
5C	592	500	2785	83.18	1.00
6A	598	500	6055	61.39	1.16
6B	597	500	4080	74.48	1.13
6C	597	500	3285	80.27	1.08
7A	652	500	4640	89.50	2.14
7B	655	500	6960	75.39	2.01

[1] 150 $cm^3 \simeq$ 130 gm

constant catalyst activity with a $2H_2/CO$ feed gas at 900 psig and $650^{o}F$. After the catalyst had equilibrated in activity, the reaction rate constant was determined to be about 2.0×10^{-6} gm mole/atm-gm cat-sec. This is slightly higher than the previous Calsicat catalyst which resulted in a value of 1.75×10^{-6}. These results with a $2H_2/CO$ ratio feed gas confirmed the work reported in the previous sections. Table IV-A-1b summarizes the data obtained. Figure IV-A-1a shows product gas composition as a function of CO conversion. Although the initial H_2/CO ratio was 2, the effluent gas at CO conversions of 97-98 percent had a H_2/CO ratio greater than 2.

The feed gas composition was switched to a 1.4 H_2/CO ratio and data points were taken at 900 psig and $650^{o}F$ (see Table IV-A-1c). The catalyst rate constant quickly equilibrated with this feed composition at the somewhat lower value of $\sim 1.74 \times 10^{-6}$ gm mole/atm-gm cat-sec. In contrast to the $2H_2/1CO$ feed gas results, this feed gas at the 97-98 percent conversion level showed an effluent gas with a H_2/CO ratio of less than 0.5 (see Figure IV-A-1b). This was probably due to the slower rate of the water gas/shift reaction which seemed to be limiting the methanation reaction (due to low levels of available H_2) at the high conversion levels. Comparison of Figures IV-A-1a and IV-A-1b indicated that at CO conversions above 90 percent, there was probably a critical feed gas H_2/CO ratio below which the H_2/CO ratio required for a polishing reactor would not be met.

Just after these runs were completed, the oil circulating pump failed due to failure of a locking retainer nut. Upon completion of repairs, the unit was put back on-stream and the effect of direct steam addition was investigated. Figure IV-A-1c shows the effect of varying the water addition rate on effluent gas composition. Note that over the given conversion range, 88-94 percent, there appears to be a critical level of water addition below which the water gas/shift reaction was limiting methanation. Above this point, about 0.15 moles steam per mole dry gas feed, the effluent gas had a H_2/CO ratio satisfactory for a polishing reactor feed gas.

Table IV-A-1b

Process Variable Scan: 66.7% H_2 - 33.3% CO (Started 8/5/75)
Calsicat Ni-230S (1/16" Spheres)*/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	VHSV Hr^{-1}	CO Conv. %	$\frac{K\ (3/R) \times 10^6}{K_H(M\rho_L)_{650°F}}$
1A	662	900	5465	99.71	4.63
2A	642	900	6095	95.08	3.39
2B	646	900	5920	91.38	2.55
3A	650	900	5980	93.32	2.69
4A	650	900	5965	90.59	2.35
4B	644	900	5885	90.71	2.53
5A	644	900	5905	88.4	2.407
6A	650	900	5325	89.15	2.02
7A	644	900	5905	86.71	2.15
7B	634	900	6315	85.96	2.55

*Catalyst Loading: 150 cm^3 = 130 grams

FIGURE IV-A-1a

COMPOSITION VS. CONVERSION

CALSICAT Ni-230S-1/16" SPHERES
900 PSIG 650°F
$2H_2/CO$ FEED GAS

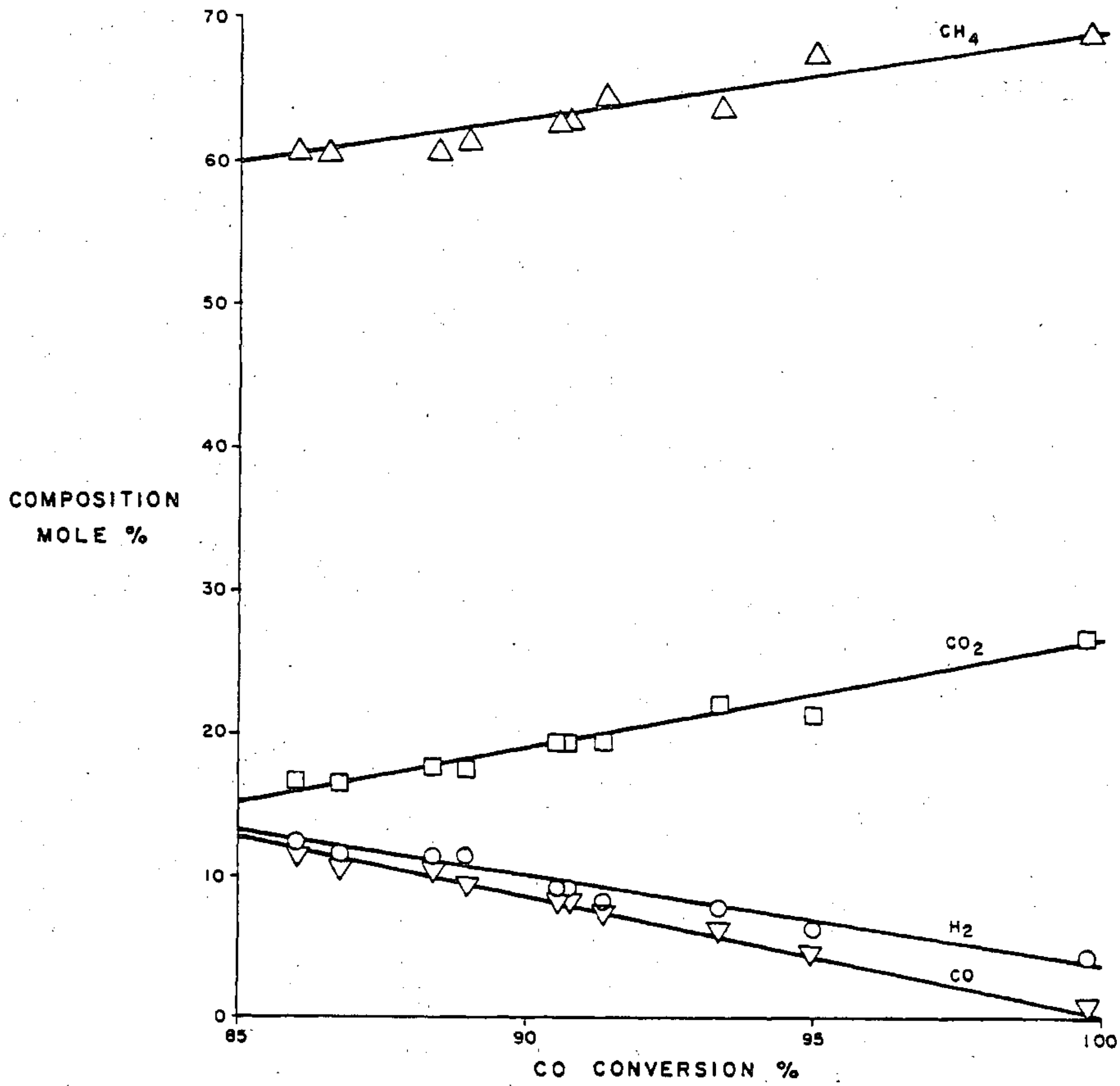


Table IV-A-1c

Process Variable Scan: 58.3% H_2 - 41.6% CO
Calsicat Ni-230S (1/16" Spheres)*/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	Moles H_2O/ Mole Dry Gas	VHSV Hr^{-1}	% CO Conv.	$\frac{K\ (3/R) \times 10^6}{K_H (M/\rho_L)_{650°F}}$
1A	654	900	0	6150	81.34	2.32
1B	656	900	0	7275	72.15	2.04
2A	646	900	0	3095	90.8	1.85
2B	648	900	0	3190	89.9	1.79
2C	648	900	0	2495	94.3	1.74
3A	654	900	0.095	2720	97.76	2.32
3B	656	900	0.085	3040	96.75	2.28
4	650	900	0.138	2865	94.4	1.96
5	664	900	0.169	3185	93.57	1.72
6A	656	900	0.210	2810	92.89	1.64
6B	650	900	0.190	3270	91.25	1.88
7	645	900	0.219	3210	92.79	1.95
8	656	900	0.299	3330	91.77	1.83
9	650	900	0.044	2695	88.29	1.65

*Catalyst Loading: 150 cm^3 = 130 grams

FIGURE IV-A-1b

COMPOSITION VS. CONVERSION

CALSICAT Ni-230S-1/16" SPHERES
900 PSIG 650°F
1.4 H_2/CO FEED GAS

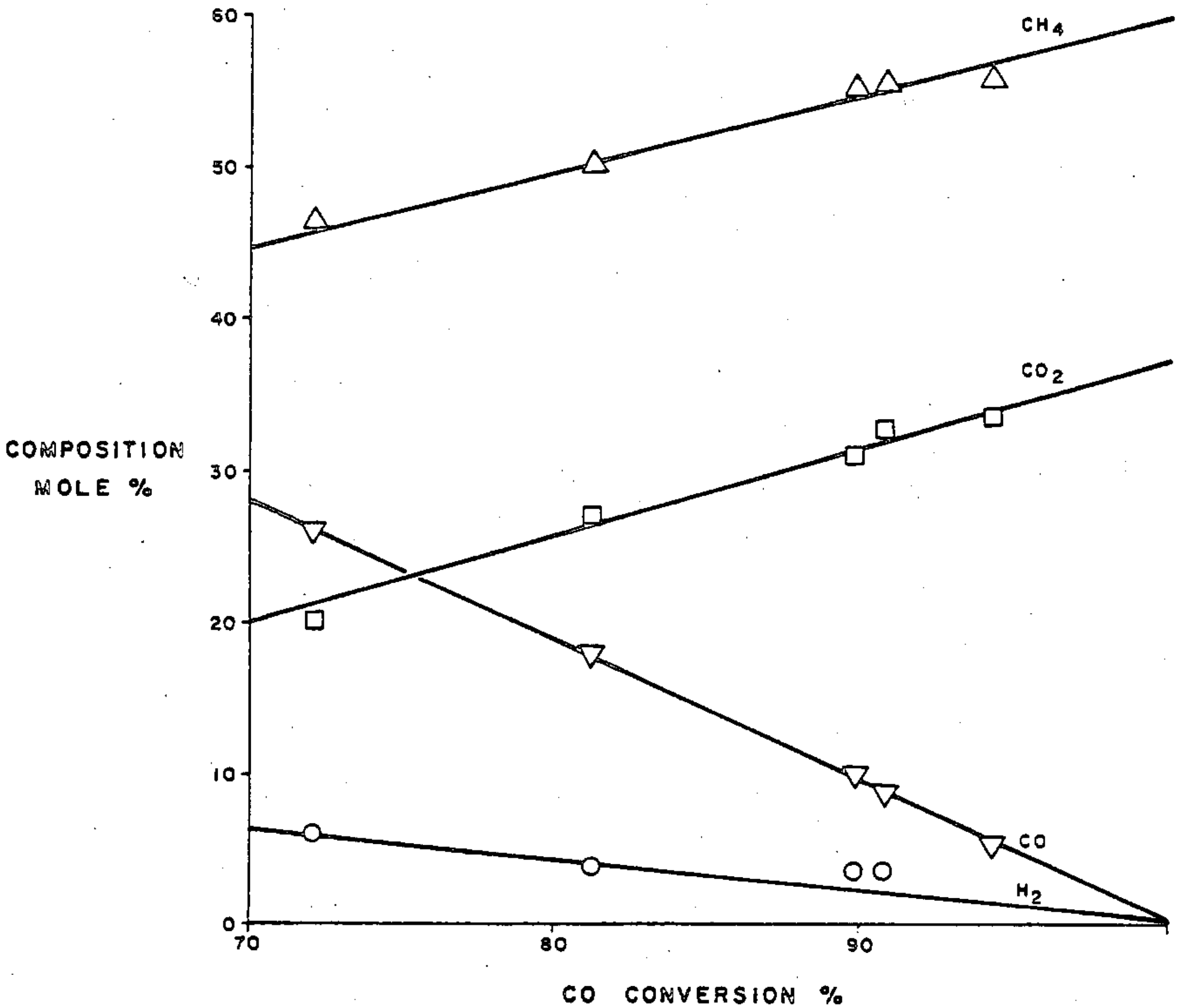
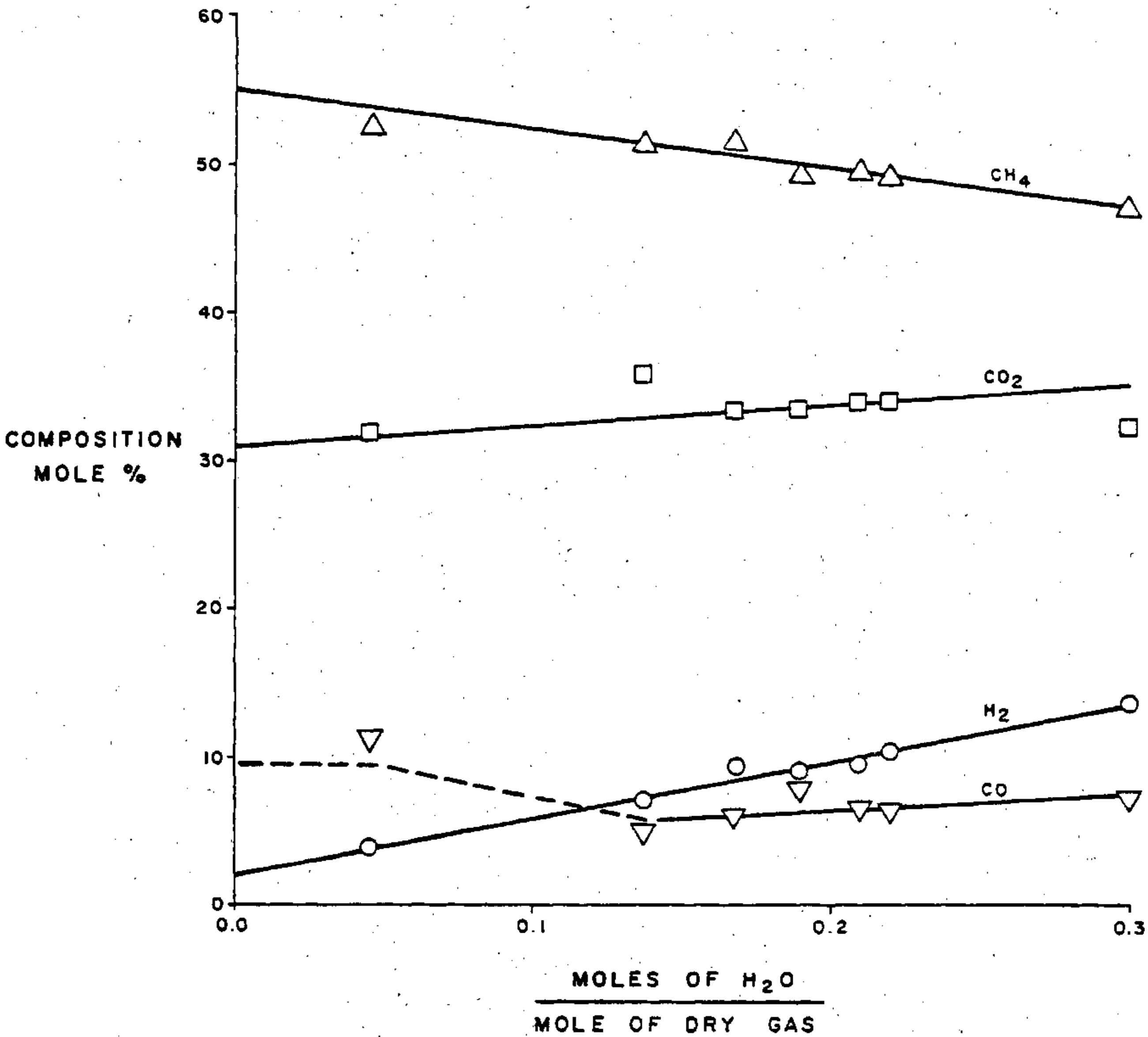


FIGURE IV-A-1c

COMPOSITION VS. WATER ADDITION RATE

CALSICAT Ni-230S-1/16" SPHERES
900 PSIG 650°F
1.4H_2/CO FEED GAS
CONVERSION ON CO 88-94%



Further attempts to obtain product gas compositions with varying water injection rates at high CO conversions were not possible due to the catalyst charge being too small to effectively reach the higher conversion levels. After shutting down the system to load a new catalyst batch, several mechanical problems were encountered with both the analytical system and the oil circulating pump.

The gas chromatographic columns were deactivated by accidental contamination of the column packing. The problems with the circulating oil pump initiated with a bearing failure which subsequently placed excessive loads on the stroke adjustment spindle causing the spindle to shear. The pump had to be disassembled and a new spindle was machined to size by a local machinery shop. While the necessary part was being machined, the oil preheat loop was removed and replaced by a new larger one, in order to handle the higher heat loads necessitated by the direct addition of water to the circulating oil.

2. Calsicat Ni-230S/Exxon Aromatic 150 Reaction Rate Studies

During the fourth quarter 1975, a series of process variable scans were initiated with the Calsicat Ni-230S (1/16" spheres)/Exxon Aromatic 150 oil system for the combined shift/methanation reaction. These runs focussed specifically on the effects of direct water injection with feed gases having initial H_2/CO ratios of 1/1 to 2/1. Table IV-A-2a summarizes the process conditions and results for the series of runs with a H_2/CO feed ratio of 1.04-1.08. Table IV-A-2b summarizes the results for the series of runs with a H_2/CO feed ratio of 1.25. Table IV-A-2c summarizes the results for the series of runs with a H_2/CO feed ratio of 0.98. The tables show the CO conversion achieved as well as the H_2/CO ratio in the reactor effluent gas. Tables IV-A-2d and IV-A-2e represent selected data from work completed under section IV-A-1 for H_2/CO feed ratios of 2.0 and 1.4 respectively.

Table IV-A-2a

Process Variable Scan: 52.1% - 50.9% H_2
48.9% - 49.1% CO

Calsicat Ni-230S (1/16" spheres)*/Exxon Aromatic 150

Pressure: 900 psig

Run No.	Temp. °F	"Contact Time"	$\frac{K(3/R) \times 10^6}{K_H(M/\rho_L)_{650°}}$	CO Conv. %	Feed H_2/CO	Effluent H_2/CO	Steam/Gas Mole Ratio
1	656	0.75	4.9	98.13	1.08	2.41	0.13
2	656	0.57	4.52	93.9	1.08	0.90	0.13
3	650	1.50	2.39	97.32	1.08	0.55	-
4	641	1.38	2.50	95.76	1.08	0.725	0.12
5	648	1.9	1.51	93.98	1.04	0.36	-
6	646	2.0	1.49	94.11	1.04	0.303	-
7	654	1.36	1.19	81.70	1.04	0.09	-
8	650	1.56	1.47	90.86	1.04	0.357	0.10
9	654	1.07	1.51	82.94	1.04	0.238	0.14
10	650	1.82	0.91	80.77	1.04	0.085	-
11	650	2.48	0.73	83.53	1.04	0.113	-
12	650	2.16	0.99	88.20	1.04	0.24	0.12
13	646	3.29	0.51	79.35	1.04	0.128	-
14	646	2.04	1.37	83.93	1.04	0.218	0.16
15	650	1.05	1.12	69.22	1.04	0.076	-
16	650	0.92	1.35	71.09	1.04	0.178	0.16
17	650	1.70	0.82	75.05	1.04	0.089	-
18	650	1.48	1.11	80.69	1.04	0.169	0.12
19	650	1.84	0.93	82.02	1.04	0.425	0.26

*Catalyst Loading: 170 cm^3 = 169.3 grams

Table IV-A-2b

Process Variable Scan: 55.5% H_2 - 45.5% CO

Calsicat Ni-230S (1/16" spheres)*/Exxon Aromatic 150

Pressure: 900 psig

ın).	Temp. °F	"Contact Time"	$\frac{K\,(3/R) \times 10^6}{K_H(M/\rho_L)_{650^o}}$	CO Conv. %	Feed H_2/CO	Eff. H_2/CO	Steam/Gas Mole Ratio
	648	2.29	3.37	99.95	1.25	-	0.17
	650	1.78	2.70	99.21		5.6	0.11
	633	2.03	2.02	96.19		1.2	0.11
	638	1.92	2.15	97.0		1.7	0.05
	650	1.77	1.37	91.31		0.65	0.09
	646	1.57	1.45	88.52		0.40	-
	650	1.53	1.55	90.16		0.78	0.13
	648	1.75	1.35	92.54		0.56	0.09
	646	1.97	1.23	90.09		0.37	-
	650	2.67	1.04	93.73		0.80	0.09
	650	2.22	1.13	91.98		0.62	0.08
	652	2.78	1.05	93.82	1.4	1.05	0.11
	652	1.83	1.09	90.06		0.77	0.12
	650	2.76	0.91	93.78		1.03	0.13
	650	2.78	1.05	92.21	1.08	0.67	0.15

*Catalyst Loading: 200 cm^3 = 194.5 grams

Table IV-A-2c

Process Variable Scan(1) - Calsicat Ni-230S(2)/Exxon Aromatic 150

Run No.	Temp. °F	VHSV Hr^{-1}	$\left(\frac{K(3/R) \times 10^6}{K_H(M/\rho_L)}\right)_{650°}$	CO Conv. Percent	Feed H_2/CO	Eff. H_2/CO	Steam/Gas Mole Ratio
1A	651	2240	3.52	97.2	0.98	0.44	-
1B	651	-	N.A.	98.9	0.98	2.29	0.105
2A	651	3245	2.4	92.2	0.98	0.17	-
2B	651	2325	3.87	98.4	0.98	2.43	0.200
3A	651	2440	2.09	87.6	0.98	0.13	-
3B	651	2445	3.00	95.0	0.98	0.85	0.145
4A	651	2420	1.80	83.7	0.98	0.11	-
4B	651	2525	1.89	85.1	0.98	0.17	0.055
5	650	2395	1.91	83.2	0.98	0.21	0.105
6	654	4460	1.85	90.3	3/1	6.88	-

(1)Pressure = 900 psig, Feed Gas Composition = 49.5% H_2, 50.5% CO

(2)Catalyst Loading = 200 cm^3 = 180 gm

Table IV-A-2d

Process Variable Scan: 66.7% H_2 - 33.3% CO $H_2/CO = 2.0$
Calsicat Ni-230S (1/16" Spheres)*/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	VHSV Hr^{-1}	CO Conv. %	$\frac{K\ (3/R) \times 10^6}{K_H (M/\rho_L)}\ 650°F$	Effluent H_2/CO
2A	642	900	6095	95.08	3.39	1.37
2B	646	900	5920	91.38	2.55	1.01
3A	650	900	5980	93.32	2.69	1.26
4A	650	900	5965	90.59	2.35	1.06
4B	644	900	5885	90.71	2.53	1.06

*Catalyst Loading: 150 cm^3 = 130 grams

Table IV-A-2e

Process Variable Scan: 58.3% H_2 - 41.6% CO $H_2/CO = 1.40$
Calsicat Ni-230S (1/16" Spheres)*/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	Moles H_2O/ Mole Dry Gas	VHSV Hr^{-1}	% CO Conv.	$\frac{K\ (3/R) \times 10^6}{K_H(M/\rho_L)_{650°}}$	Effluent H_2/CO
1A	654	900	0	6150	81.34	2.32	0.22
1B	656	900	0	7275	72.15	2.04	0.24
2A	646	900	0	3095	90.8	1.85	0.45
2B	648	900	0	3190	89.9	1.79	0.41
2C	648	900	0	2495	94.3	1.74	0.89
3A	654	900	0.095	2720	97.76	2.32	2.63
3B	656	900	0.085	3040	96.75	2.28	2.04
4	650	900	0.138	2865	94.4	1.96	1.36
5	664	900	0.169	3185	93.57	1.72	1.58
6A	656	900	0.210	2810	92.89	1.64	1.42
6B	650	900	0.190	3270	91.25	1.88	1.13
7	645	900	0.219	3210	92.79	1.95	1.61
8	656	900	0.299	3330	91.77	1.83	1.91
9	650	900	0.044	2695	88.29	1.65	0.34

*Catalyst Loading: 150 cm^3 = 130 grams

These data have been used in the present correlations. Figures IV-A-2a, b, c & d, show the catalyst activity as a function of time for these sets of runs. As shown, the catalyst activity declined to an equilibrium value after about 50 hours on-stream. Figures IV-A-2e, f, g, h, relate the initial catalyst performance to the equilibrium value. This activity decay function was used to evaluate the data. The catalyst used throughout this series of process variable scans was Calsicat Ni-230S. Different loadings were used in order to facilitate operation at desired conversion levels. The results, as presented in the tables and figures, were correlated in terms of the first order reaction model (a):

$$\ln\left(\frac{1}{1-X_T}\right) = \frac{K}{K_H(M/\rho_L)} * \frac{(P_T - P^*) \quad W}{F^o \;(1 \;\frac{(R+1)}{2}\; Y^o{}_{CO})} * \frac{R}{3} * \frac{1}{F(t)} * \frac{1}{\left(1+\frac{S}{G}\right)} \quad (1)$$

(a) See previous reports for definition of terms.

The term 3/R in the above expression is used to correlate results for feed gas compositions where the initial H_2/CO ratio is less than 3/1. Also inlcuded in the above expression is the term $1/\left(1+\frac{S}{G}\right)$ which corrects for the dilution of the feed gas by the injected steam. Figure IV-A-2i shows the data plotted as a function of CO conversion versus "contact time" for the runs where the initial hydrogen to carbon monoxide ratio was 1.04. Figure IV-A-2j shows the same thing for the runs where the initial H_2/CO ratio was 1.25. Figure IV-A-2k shows the results for the runs where the initial H_2/CO ratio was 1.4, and Figure IV-A-2l shows the results for the runs where the initial H_2/CO ratio was 0.98.

Figures IV-A-2m, n and o, show the effluent gas H_2/CO ratio as a function of CO conversion, with and without steam addition. Figure IV-A-2p shows the H_2/CO ratio as a function of CO conversion for a feed gas where the initial H_2/CO ratio was 2/1. This figure was based on data reported in section IV-A-1, but repeated here to show the effect of initial H_2/CO ratio.

FIGURE IV-A-2a

CATALYST ACTIVITY VS. HOURS ON STREAM

CALSICAT NI-230S/EXXON 150
900 PSIG / 650°F
1.04 H_2/CO FEED GAS

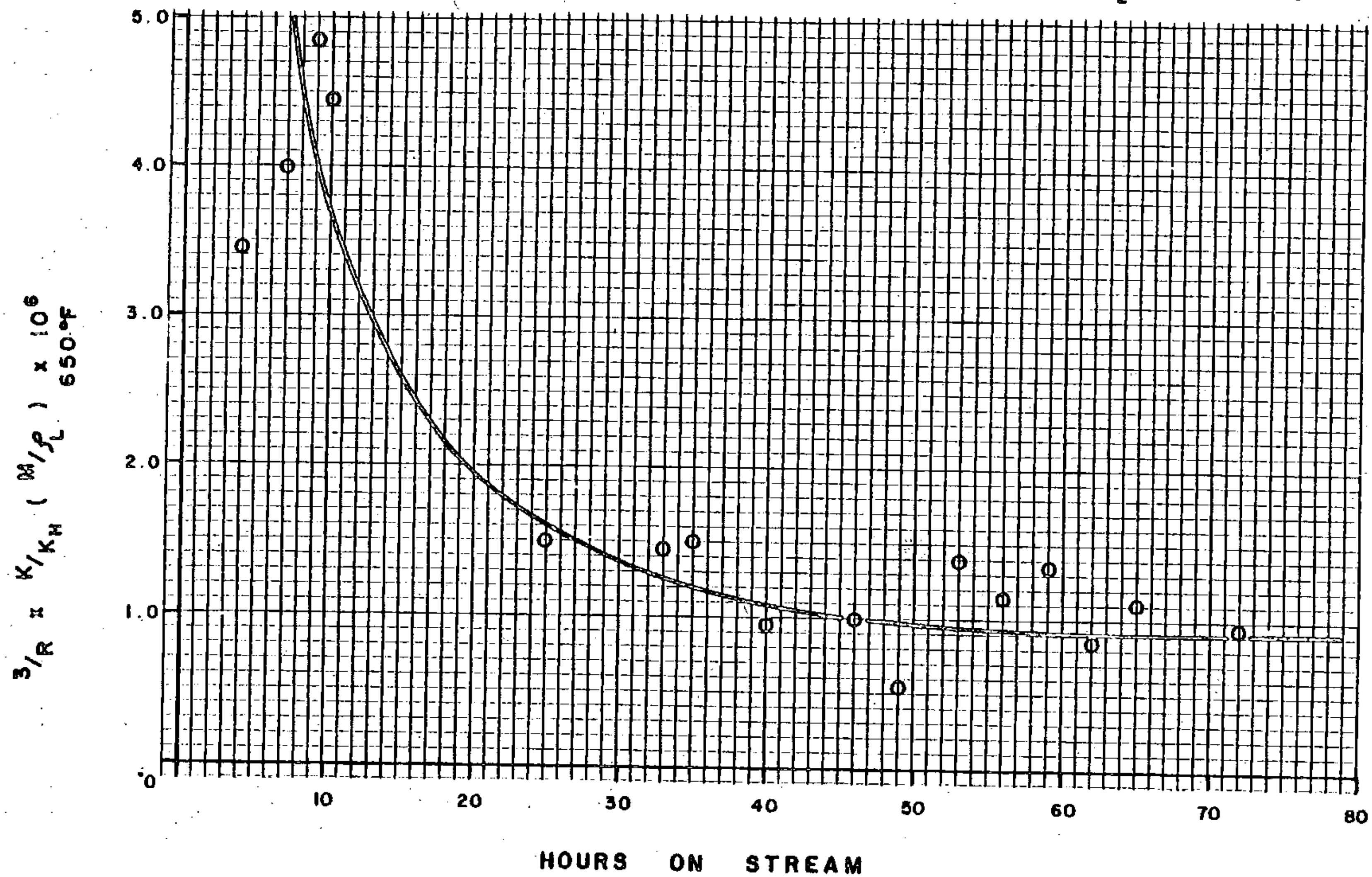


FIGURE IV-A-2b

CATALYST ACTIVITY VS. HOURS ON STREAM

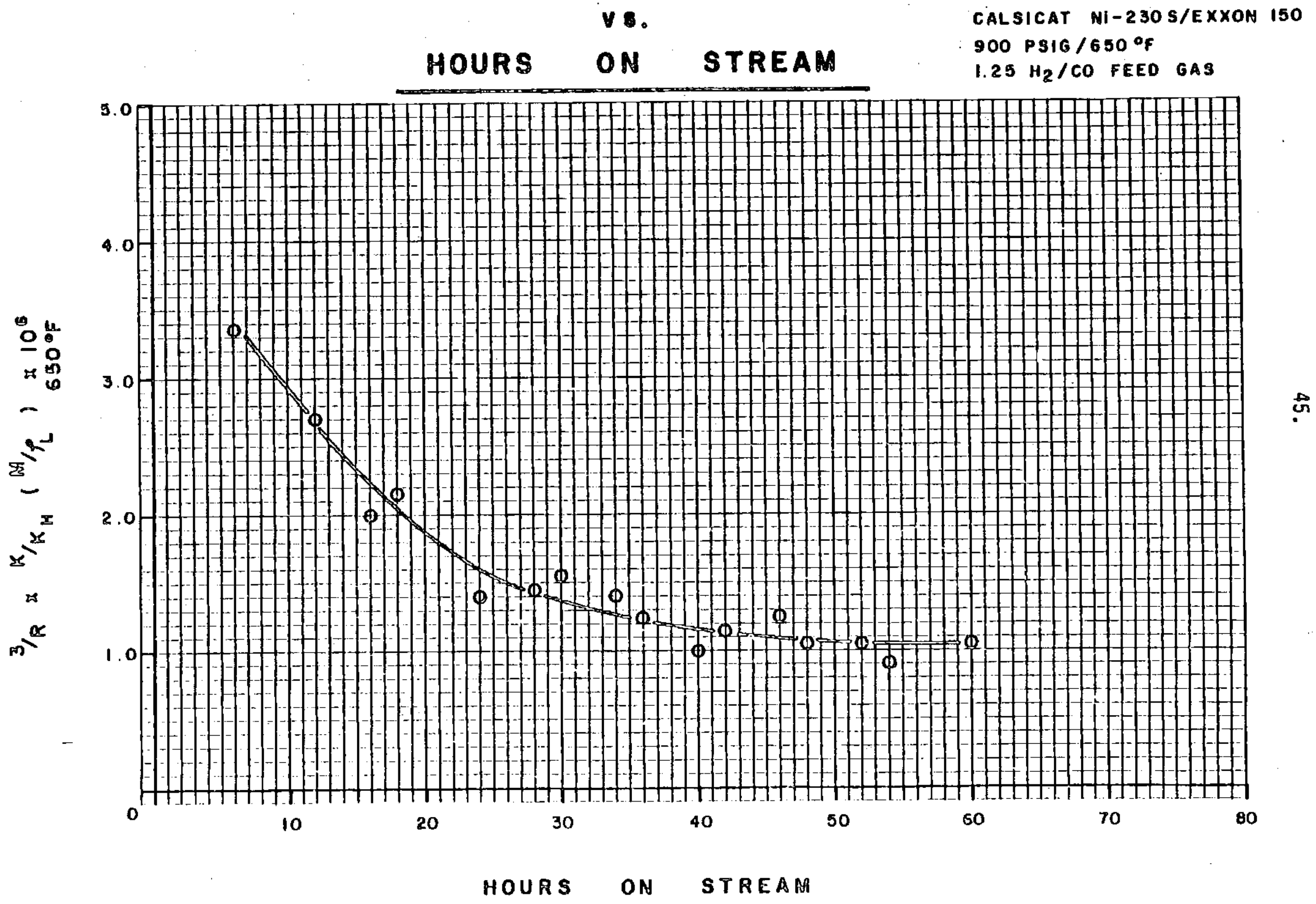


FIGURE IV-A-2c

CATALYST ACTIVITY

VS.

HOURS ON STREAM

CALSICAT NI-230S/MINERAL OIL
900 PSIG / 650 °F

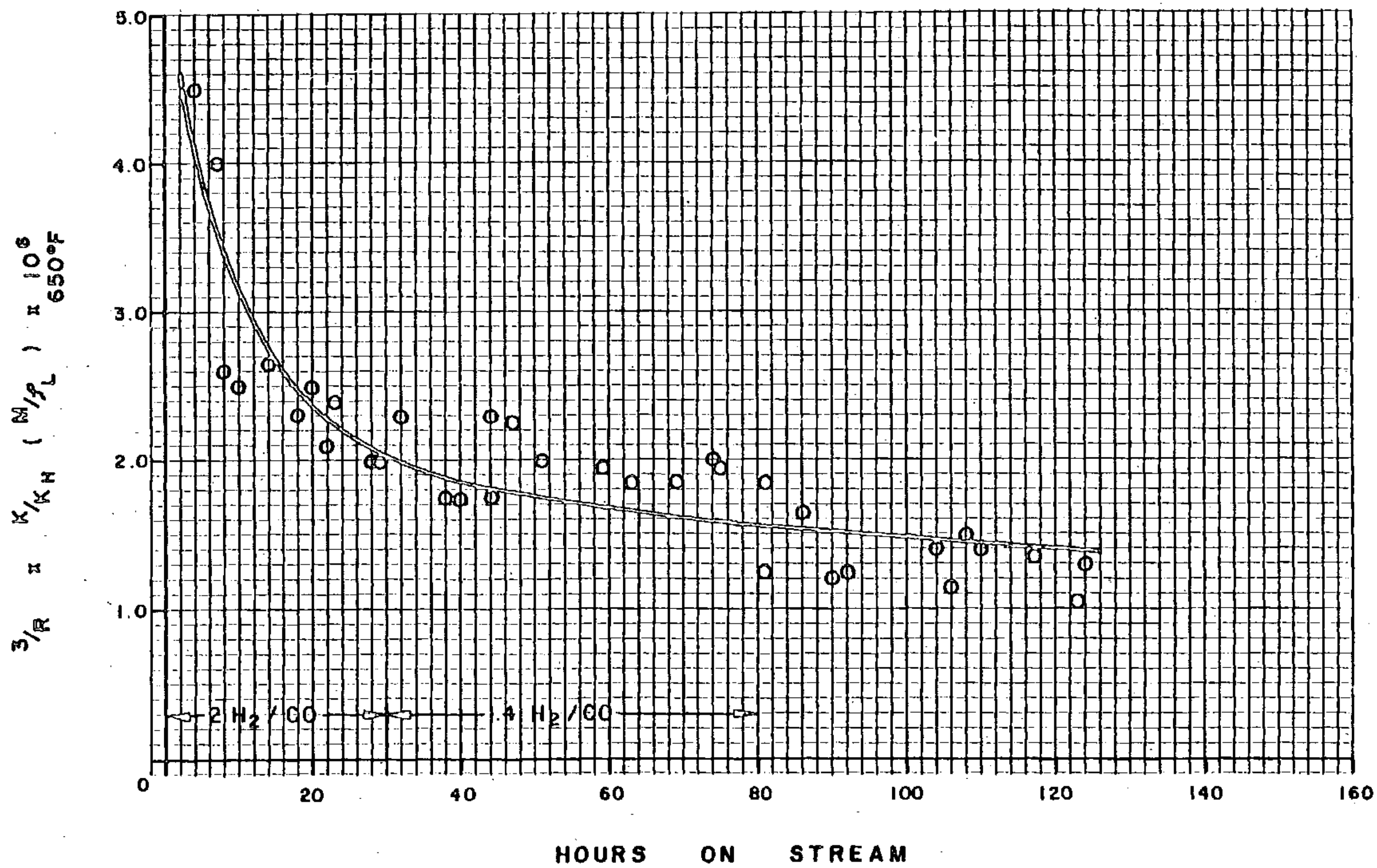


FIGURE IV-A-2d
CATALYST ACTIVITY
VS.
HOURS ON STREAM

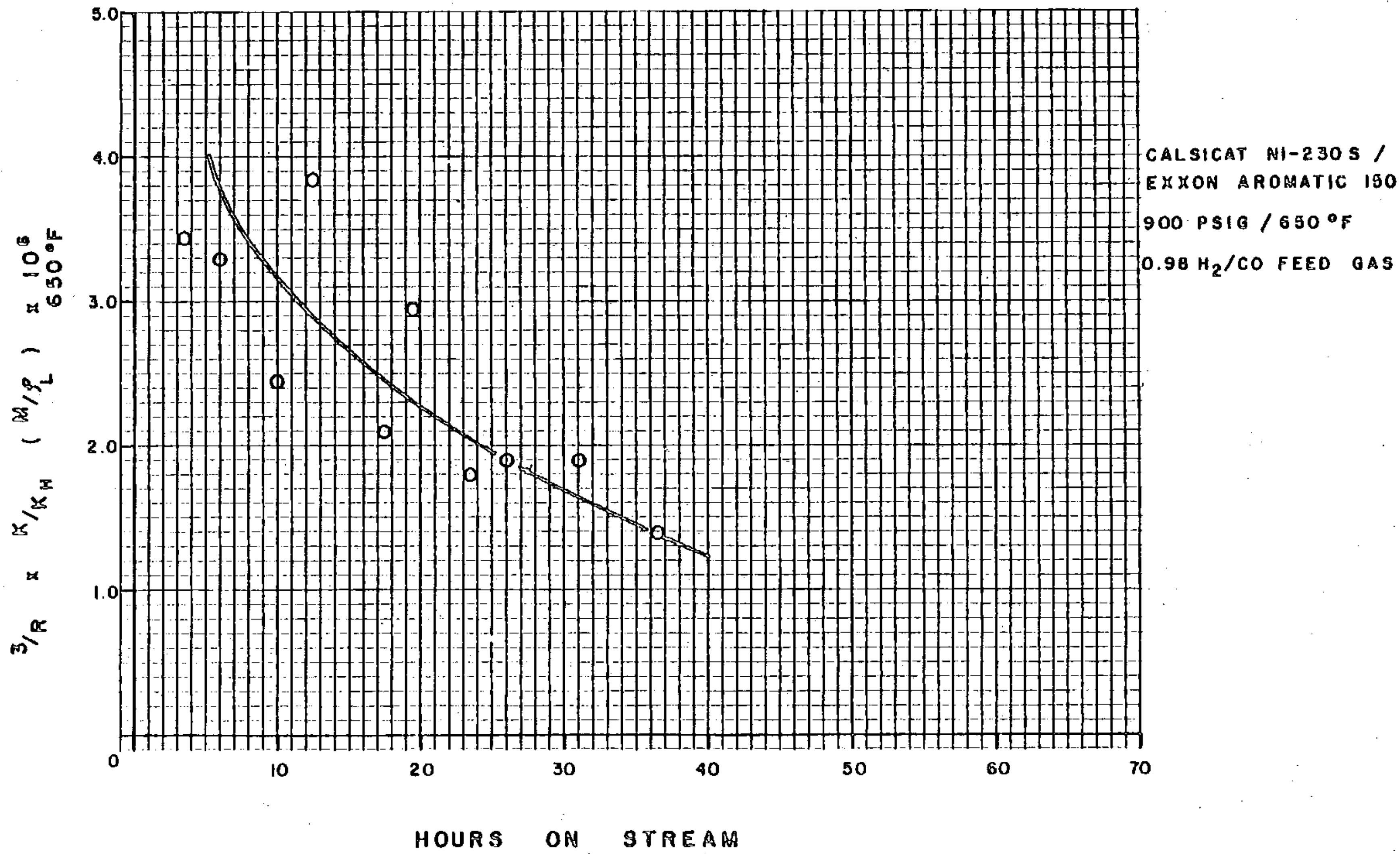


FIGURE IV-A-2e

ACTIVITY CORRECTION VS. HOURS ON STREAM