FIGURE IV-A-2f

ACTIVITY CORRECTION

VS.

HOURS ON STREAM

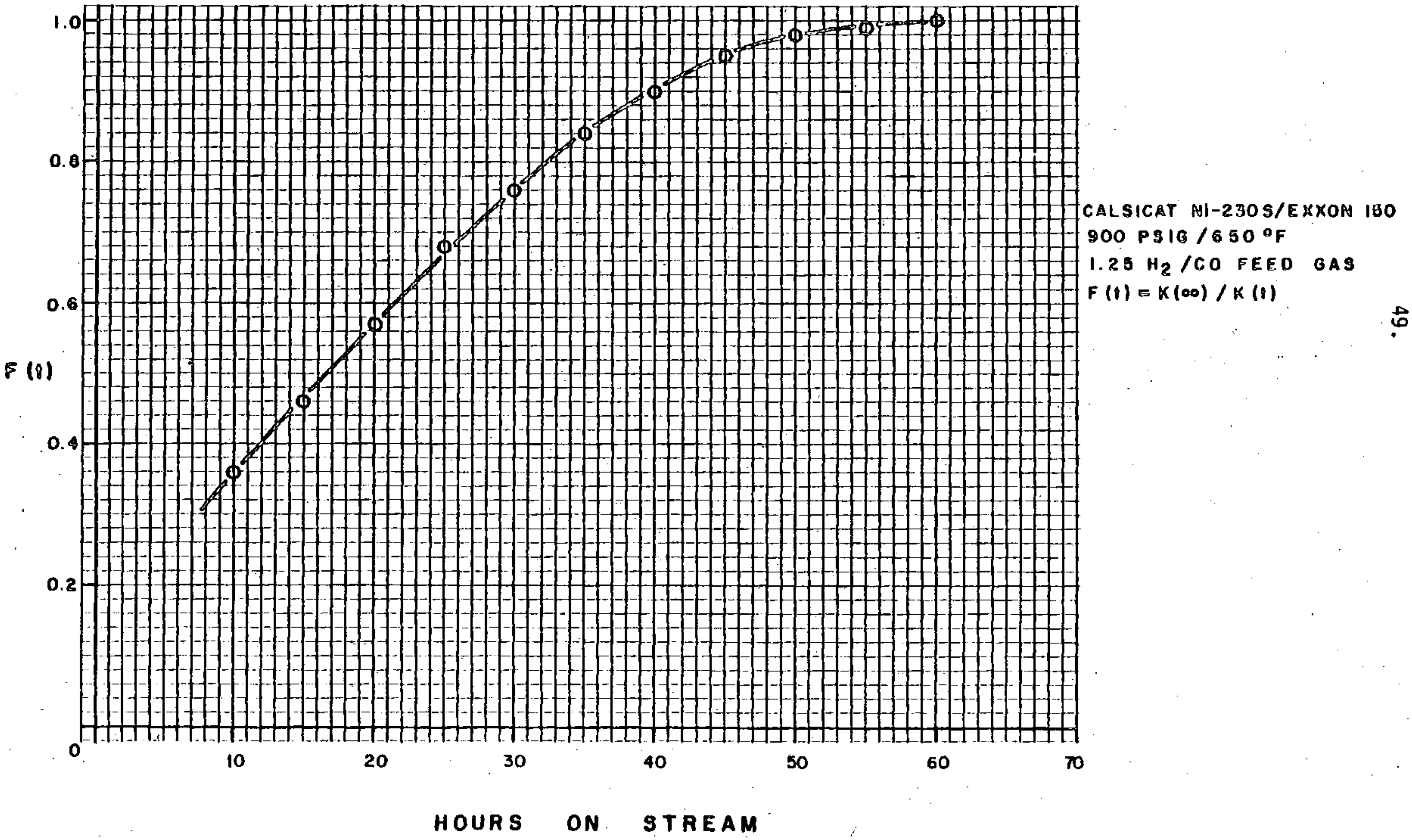


FIGURE IV-A-2g

ACTIVITY CORRECTION
VS.
HOURS ON STREAM

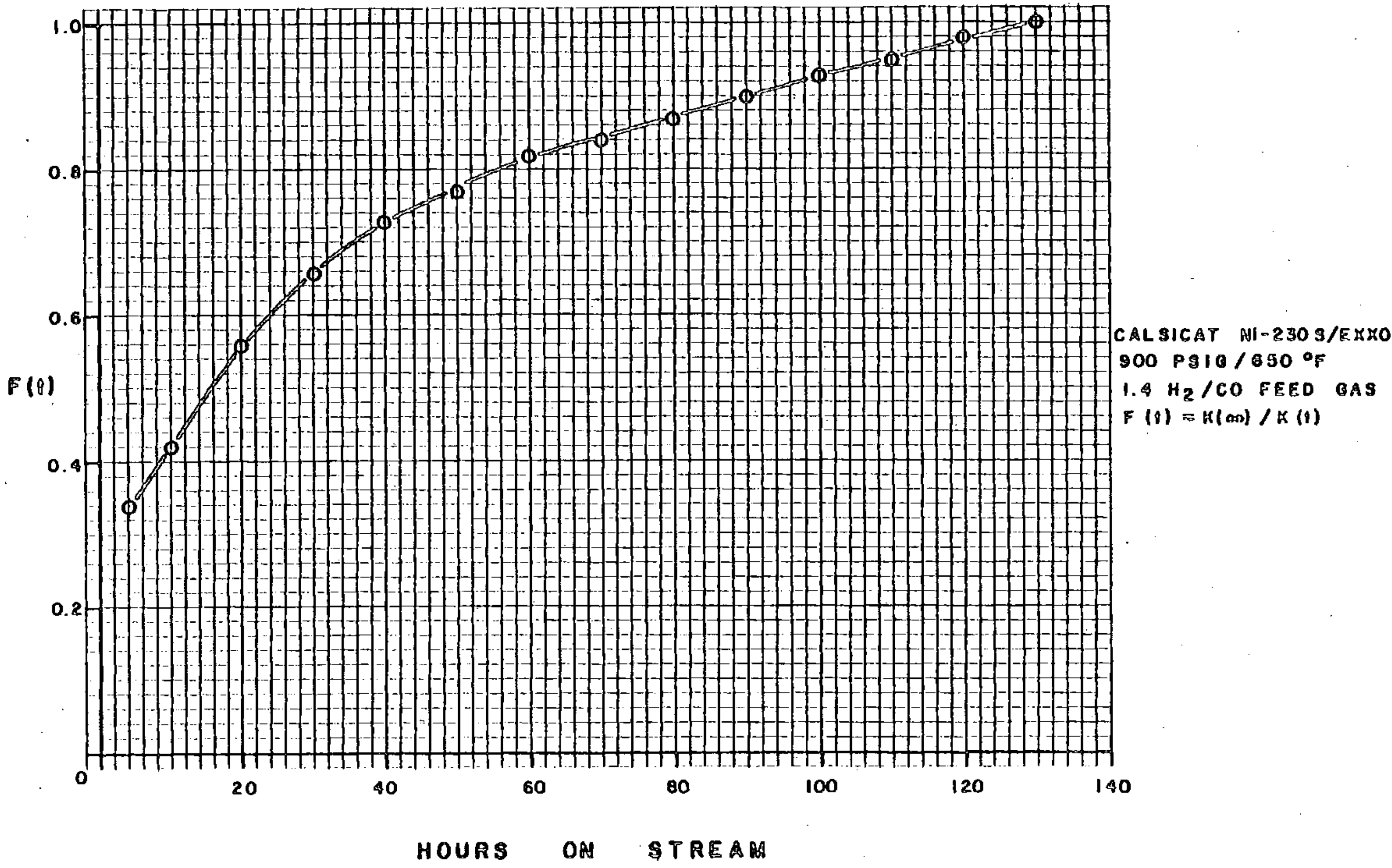
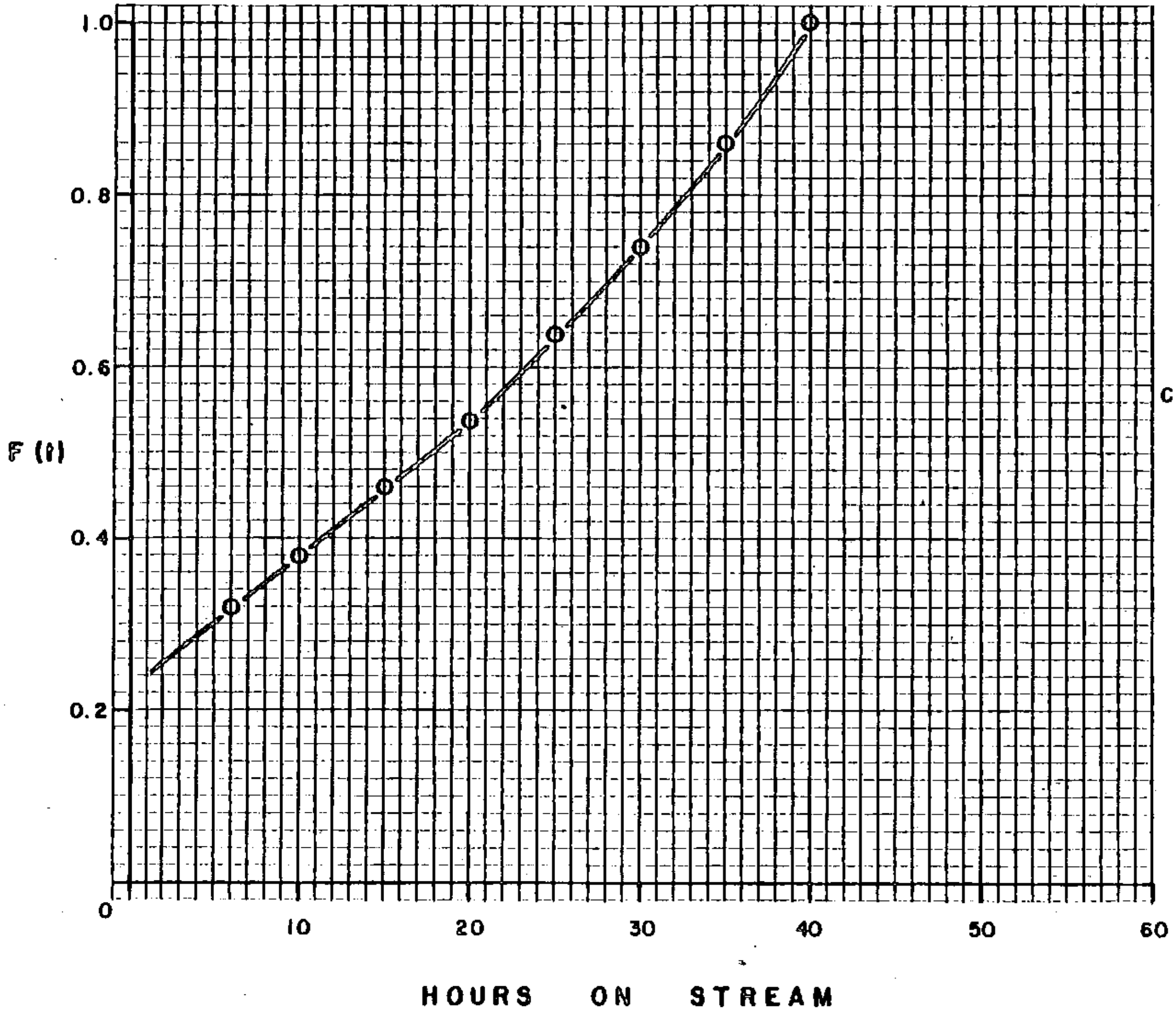


FIGURE IV-A-2h

ACTIVITY CORRECTION
VS.
HOURS ON STREAM



CALSICAT NI-230 S/EXXON AROMATIC 150
900 PSIG / 650 °F
0.98 H_2 / CO FEED GAS
F (t) = K (∞) / K (t)

FIGURE IV-A-21

CONVERSION VS. CONTACT TIME

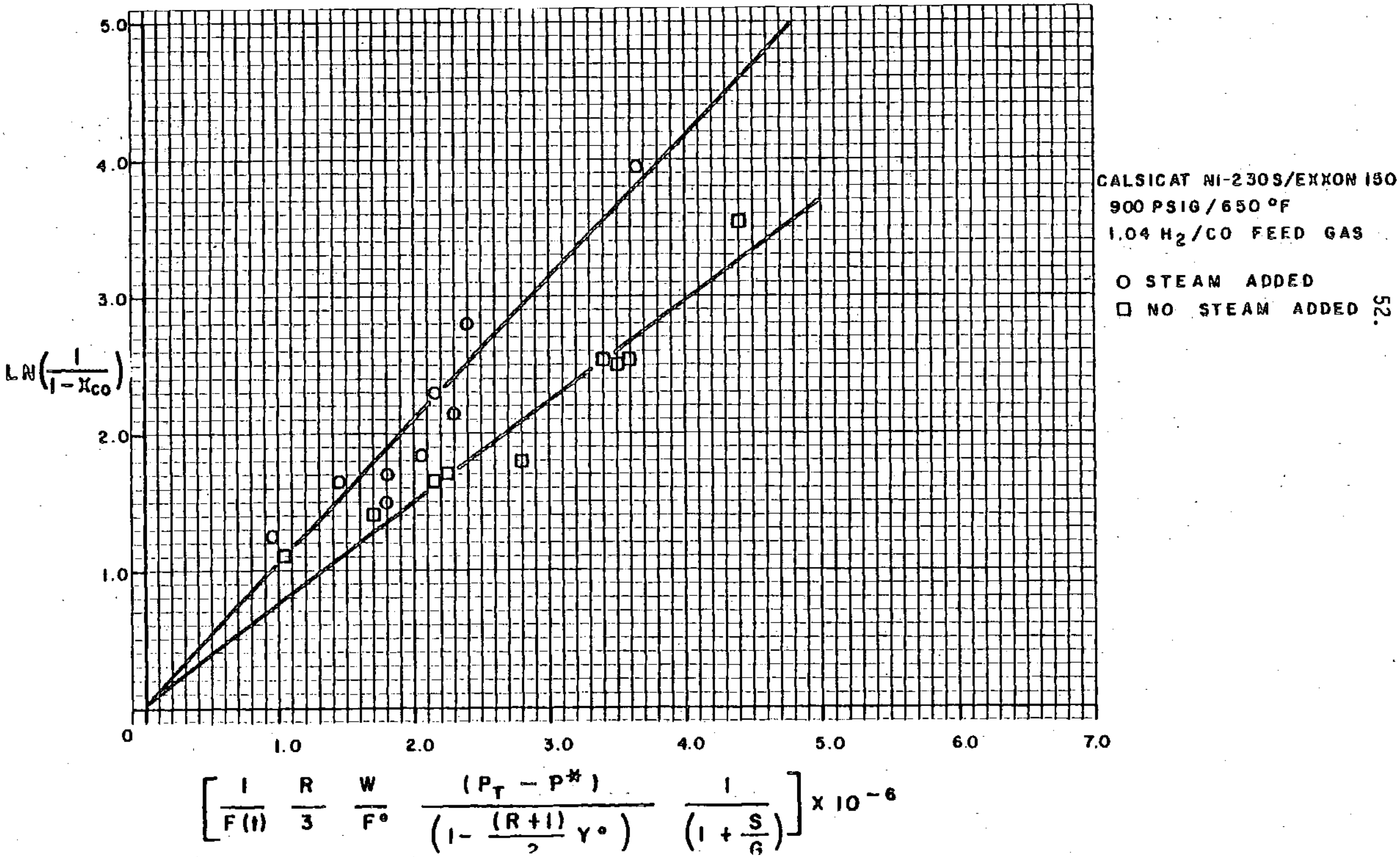
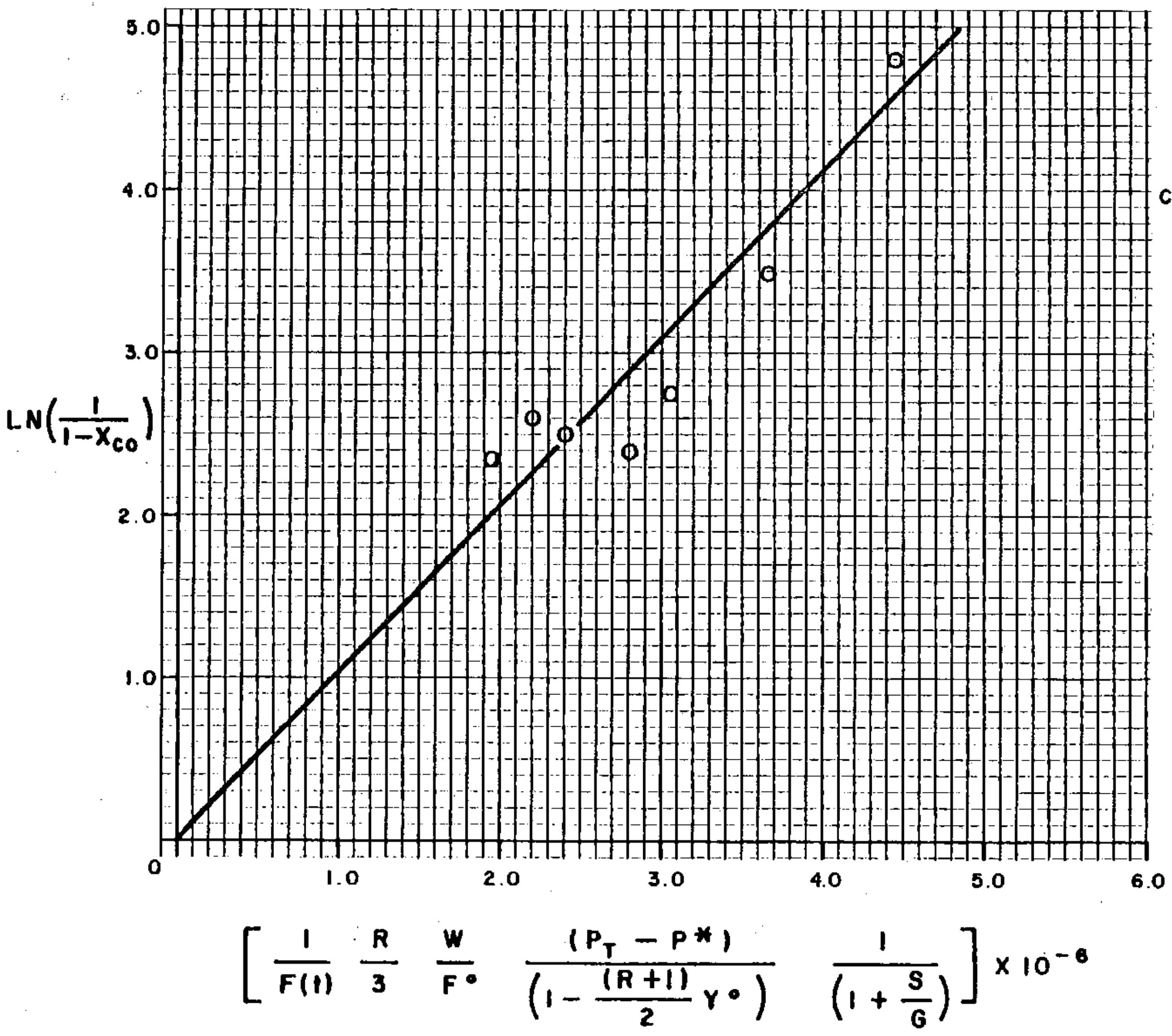


FIGURE IV-A-21

CONVERSION vs. CONTACT TIME



CALSICAT NI-230 S/EXXON 150
900 PSIG / 650 °F
1.25 H_2/CO FEED GAS
WITH STEAM ADDED

FIGURE IV-A-2k

CONVERSION vs. CONTACT TIME

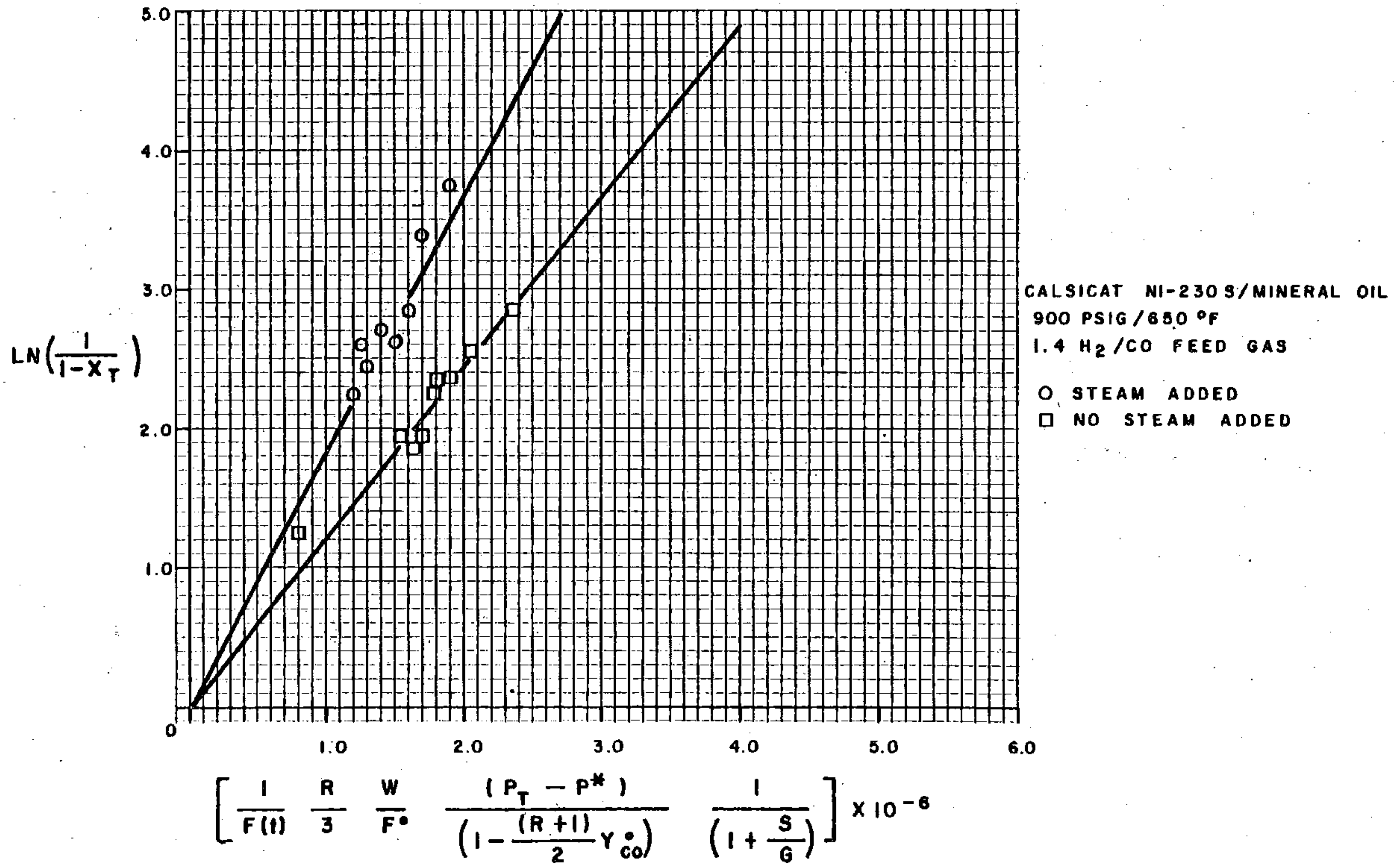


FIGURE IV-A-21

CONVERSION vs. CONTACT TIME

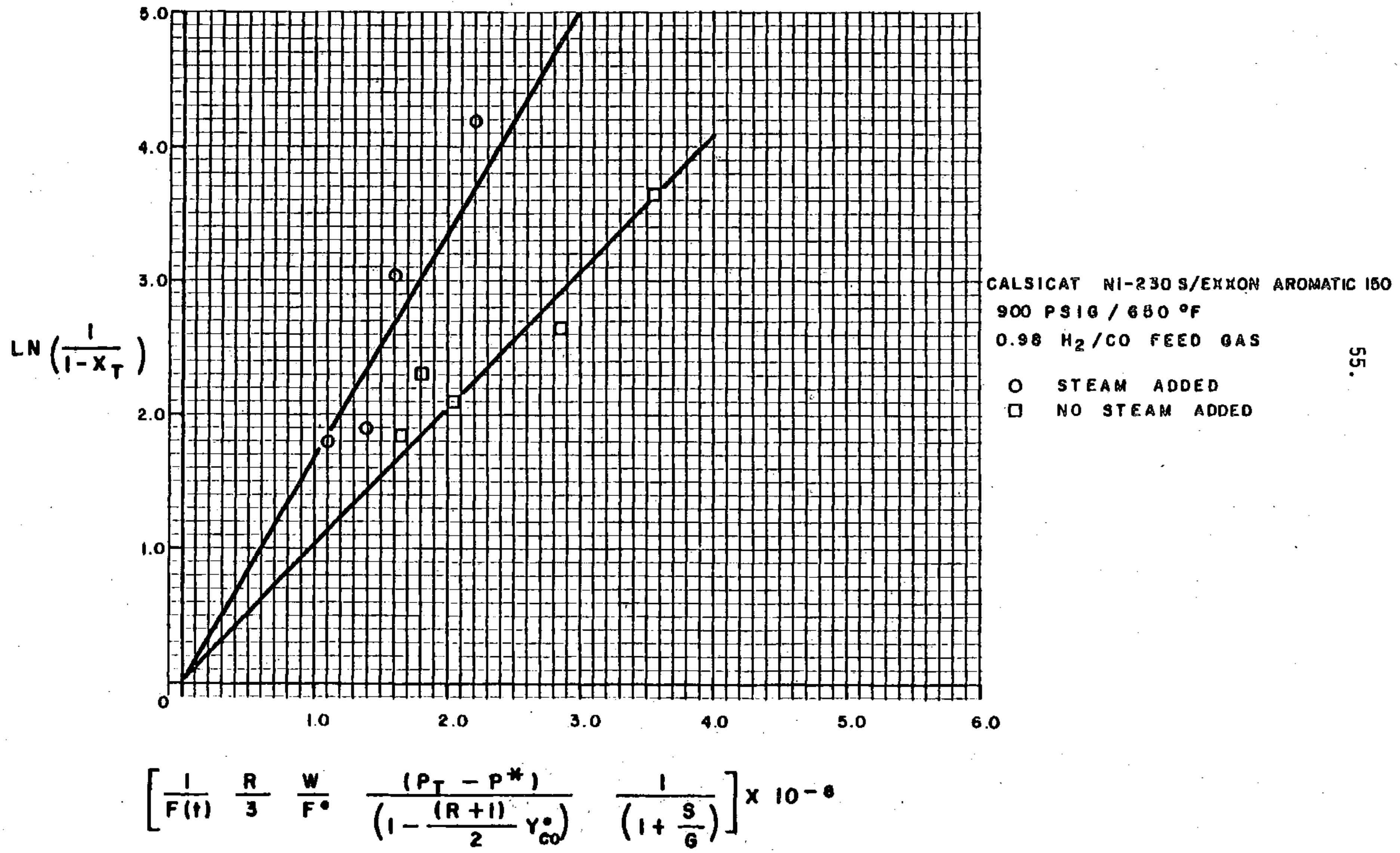


FIGURE IV-A-2m

EFFLUENT H_2/CO RATIO vs. CO CONVERSION

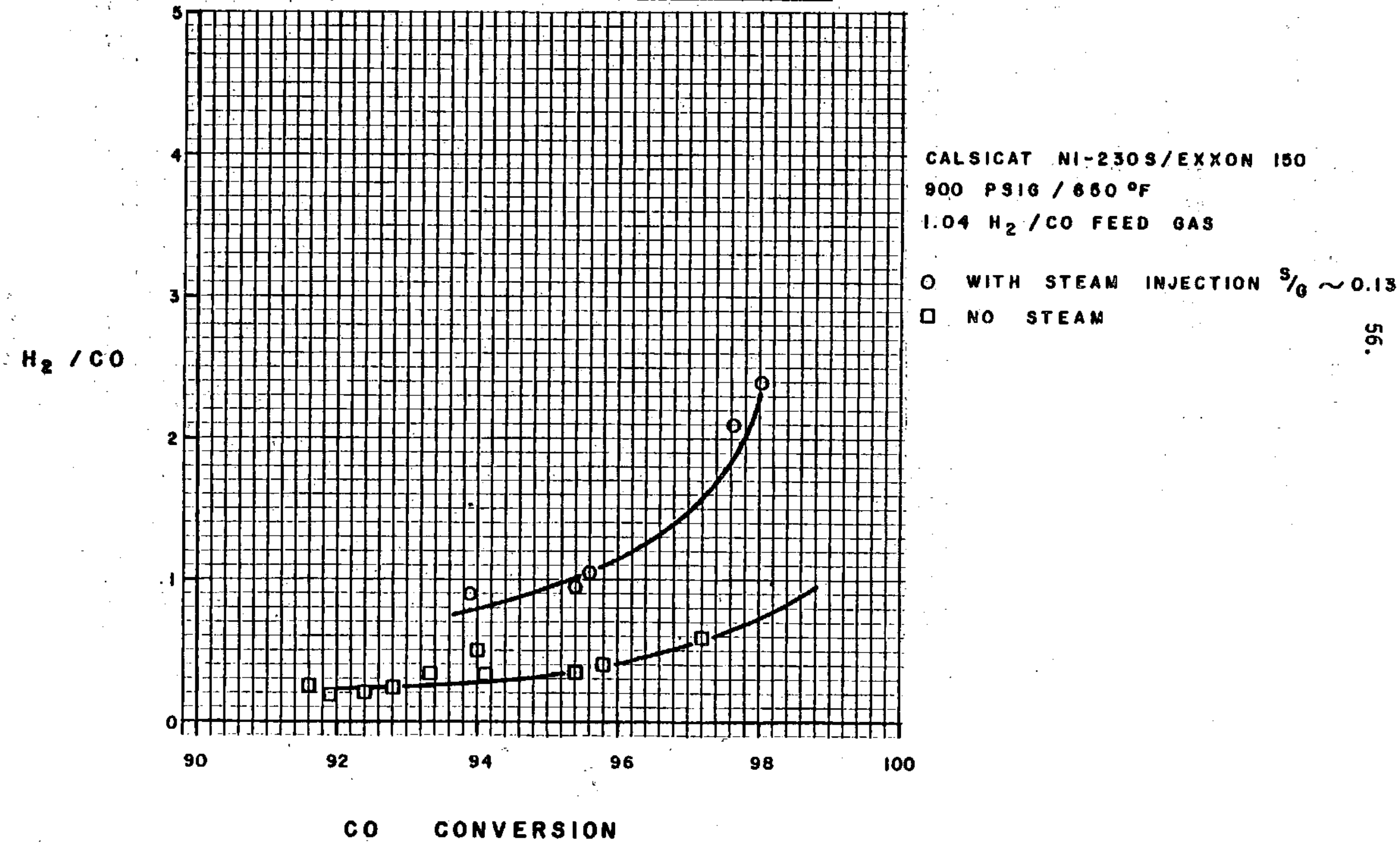


FIGURE IV-A-2n

EFFLUENT H_2/CO RATIO
VS.
CO CONVERSION

CALSICAT NI-230S/EXXON 150
900 PSIG/650 °F
1.25 H_2/CO FEED GAS
WITH STEAM INJECTION S/G ~ 0.1

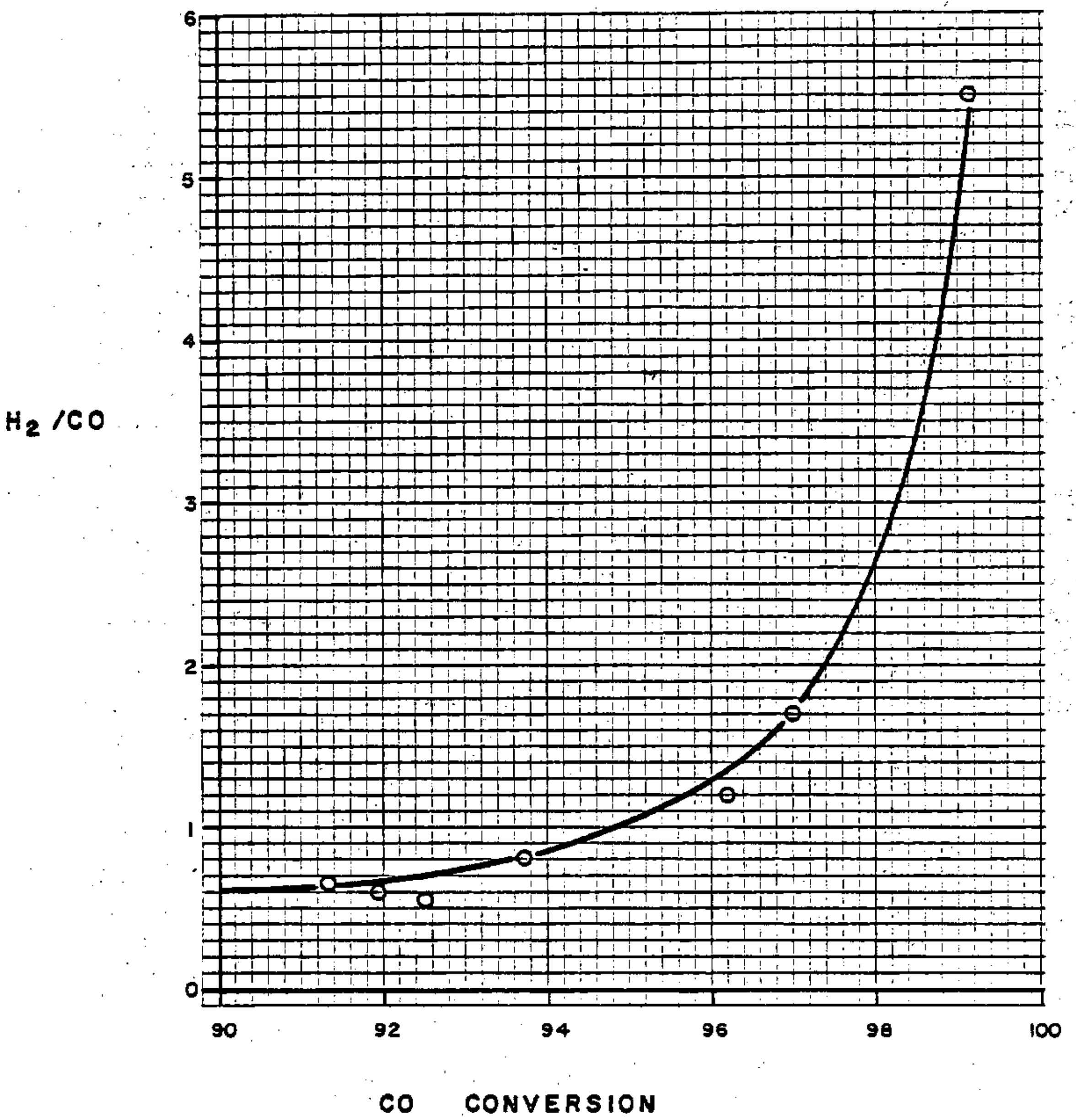


FIGURE IV-A-2a

EFFLUENT H_2/CO RATIO

VS.

CO CONVERSION

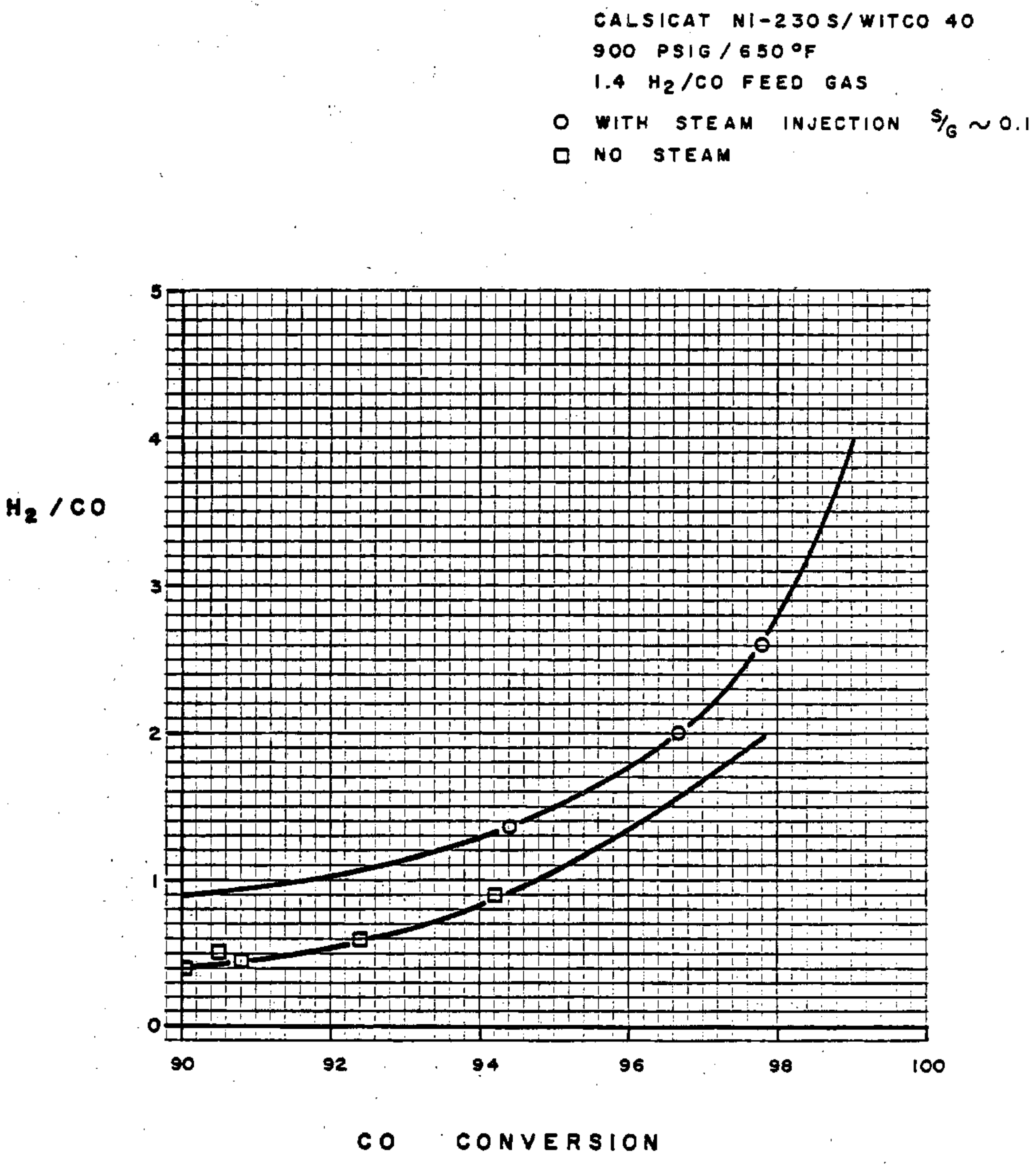
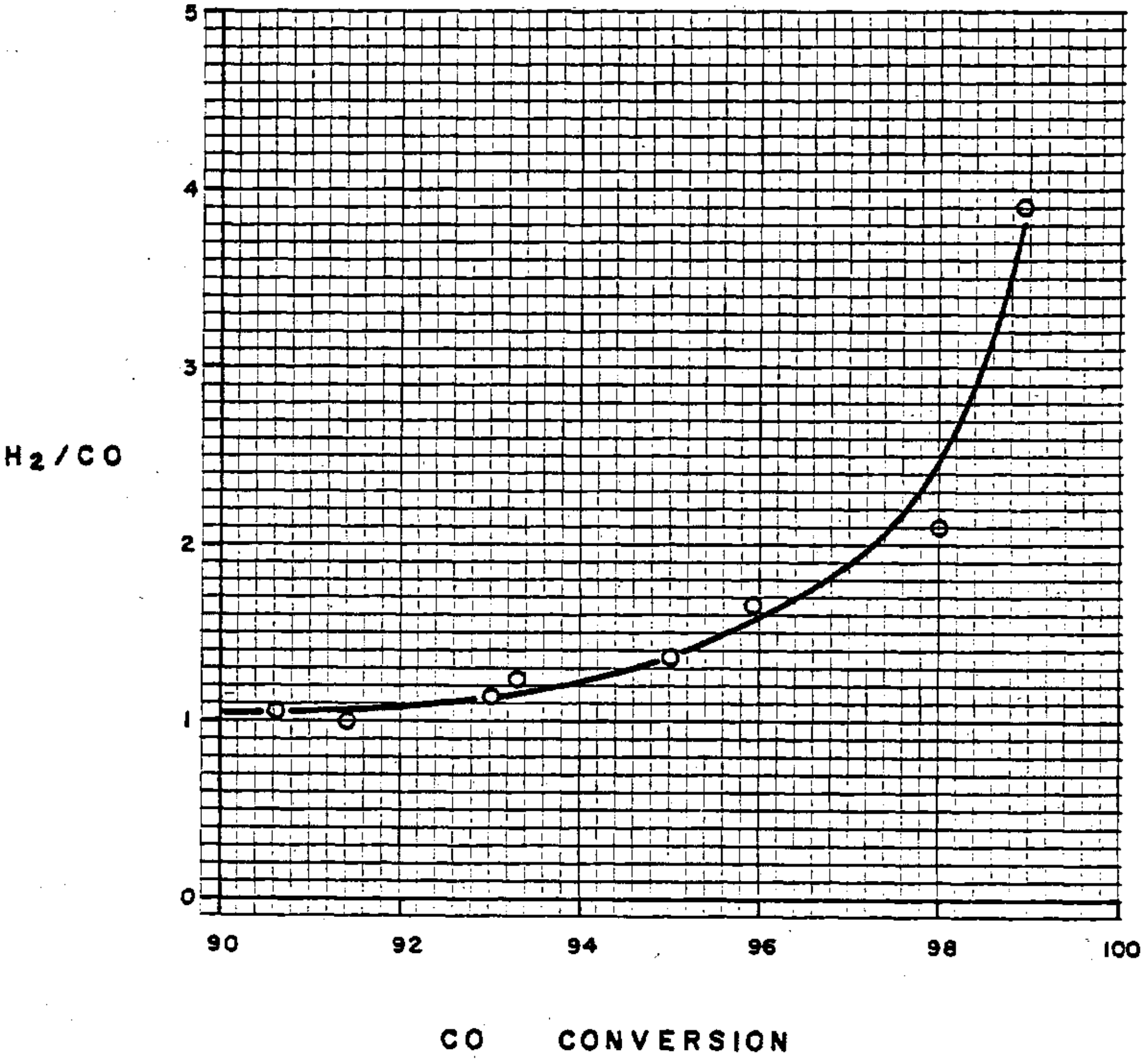


FIGURE IV-A-2p

EFFLUENT H_2/CO RATIO VS. CO CONVERSION

CALSICAT Ni-230 S/WITCO 40
900 PSIG / 650 °F
2 H_2/CO FEED GAS
NO STEAM



In general, the results revealed a dramatic difference in system productivity due to direct water injection. The data for all these runs which had a H_2/CO ratio in the feed gas of less than 2/1 revealed the following:

- No water injection gave a lower overall reaction rate due to the slower water gas shift reaction which supplied the hydrogen for the methanation reaction.
- When operating at high CO conversion levels without water injection, the effluent gas was deficient in hydrogen and unsuitable as a feed to a polishing reactor.
- The addition of water increased the overall reaction rate to a higher level by promoting the water gas shift reaction. Thus the methanation reaction was no longer limited by available hydrogen, and proceeded at a faster rate.
- The addition of water caused a pronounced change in effluent gas composition, particularly increasing the exit gas H_2/CO ratio.

At the time there were no design criteria for the H_2/CO ratio in the feed gas to a polishing reactor. However, experience with the present polishing reactor operating with a $2H_2/CO$ feed gas ratio indicated that this ratio may be acceptable and not present any problems. Table IV-A-2f showed that a H_2/CO effluent ratio of 2/1 could be achieved with a 1.4 H_2/CO feed gas with the appropriate rate of water addition.

The 1.04 and 1.25 H_2/CO feed gases, even with water injection of 0.1 mole H_2O/mole dry gas, yielded effluent gases deficient in hydrogen. Increasing the water injection rate should increase the H_2/CO ratio in the effluent stream to an acceptable level.

Table IV-A-2f

Comparison of Exit H_2/CO Ratio for Runs With and Without Water Injection

(97% Design Conversion Level S/G ~0.1)

Feed Gas H_2/CO	Exit Gas H_2/CO	
	No Water	Water Added
0.98	0.44	2.3
1.04	0.5	1.5
1.25	Not Available	1.75
1.4	1.65	2.15
2.0	1.85	Not Available

Figure IV-A-2q summarizes all the data by showing the effect on conversion of varying the steam to dry gas ratio for a 1.4 H_2/CO ratio feed gas. The reaction rate constant (slope of conversion vs. contact time) increased with increasing steam to dry gas feed ratio and then began to decrease indicating a maximum has been reached. Figure IV-A-2r shows more clearly that a maximum catalyst activity occurred at a S/G ratio of 0.085 mole H_2O/mole dry gas. Figure IV-A-2s shows the effect of varying the steam to dry gas ratio for the runs with an initial H_2/CO feed ratio of 0.98. Figure IV-A-2t shows that for this feed gas, a maximum steam addition rate was not achieved.

With the above results, it seemed reasonable to conclude that there was an optimum water addition rate, below which the water gas shift reaction was limiting the methanation reaction due to insufficient free hydrogen. Above the optimum water addition rate, there appeared to be a dilution effect of the feed stream by the added unreacted steam thereby decreasing the overall rate.

The results indicated that steam addition to the liquid phase combined shift/methanation reactor dramatically affected the effluent compositions. For feed gases with a H_2/CO ratio less than 2, steam addition would be required in order to maintain an effluent hydrogen concentration satisfactory for a polishing reactor.

3. Engelhard Catalysts

Also during the fourth quarter 1975, two different Engelhard catalyst formulations were tested. Table IV-A-3a summarizes the process variable scan on an Engelhard 3011F (3/32" spheres, 30 percent Ni on alumina) Exxon Aromatic 150 oil system. At 650°F and 900 psig, the catalyst exhibited a low initial activity and a gradual decline in activity as a function of time on-stream. (See Figure IV-A-3a).

FIGURE IV-A-2q

CONVERSION vs. CONTACT TIME

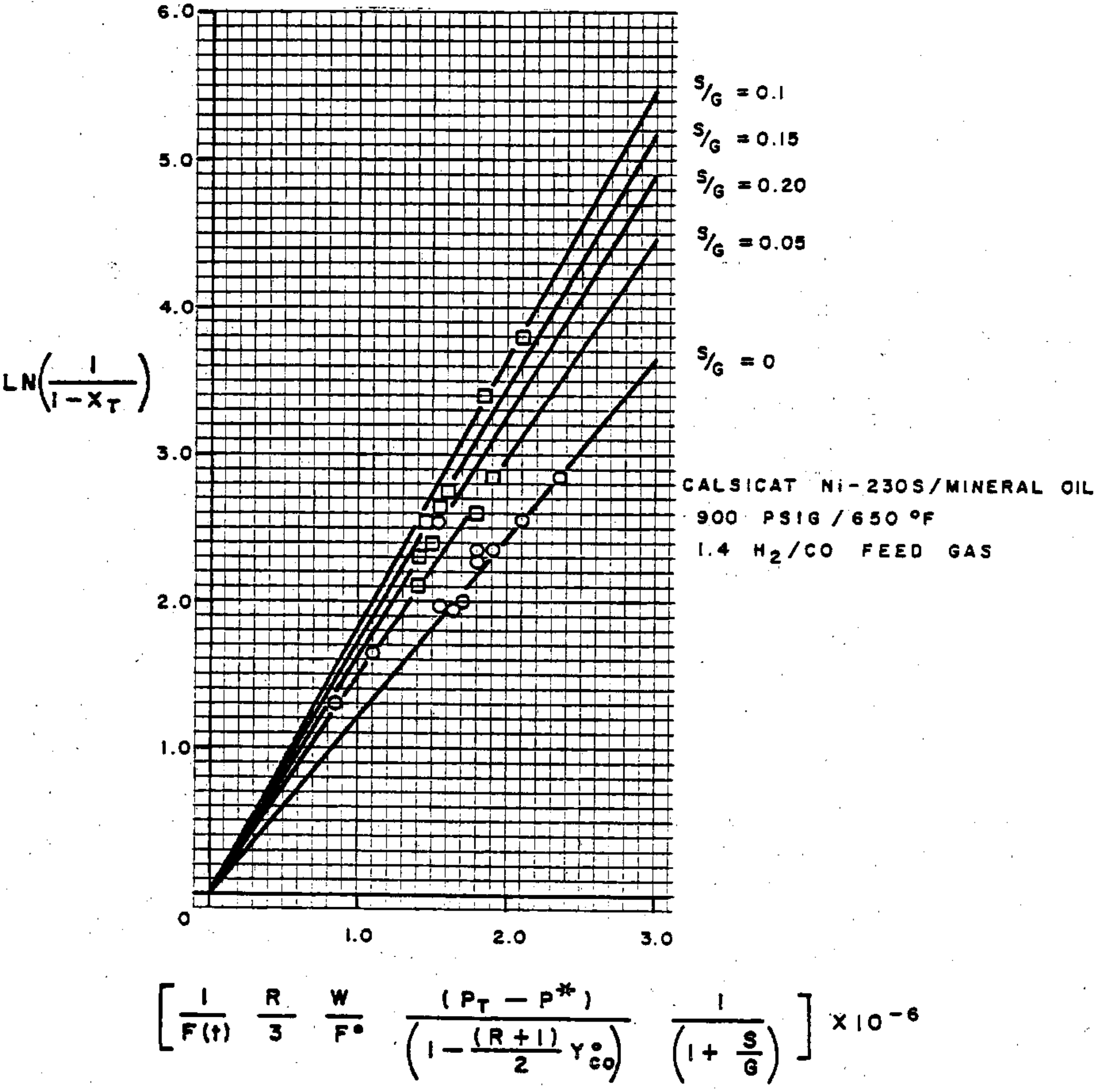
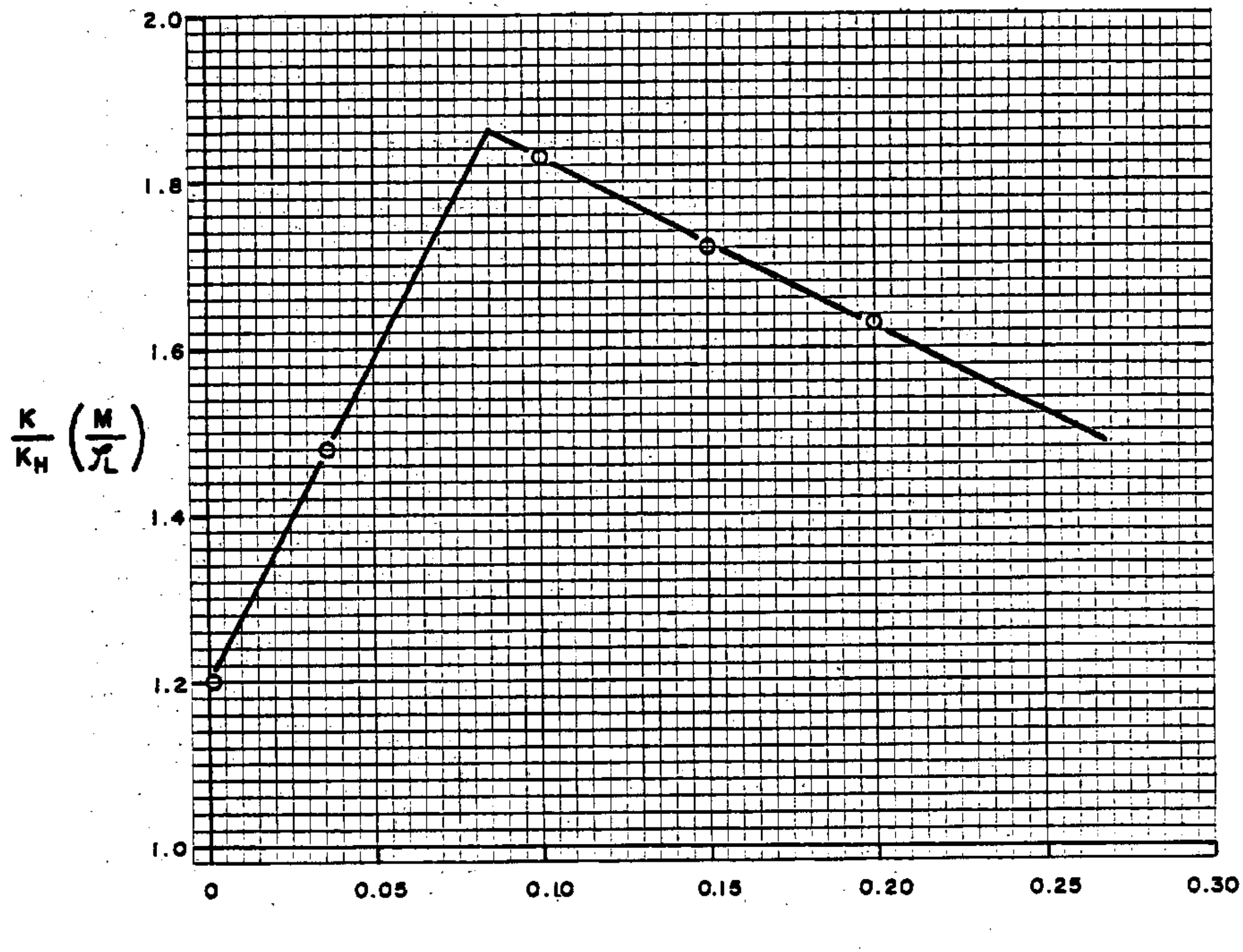


FIGURE IV-A-2r

REACTION RATE CONSTANT vs. STEAM TO GAS RATIO

CALSICAT NI-230 S / MINERAL OIL
900 PSIG / 650 °F
1.4 H_2/CO FEED GAS



STEAM / DRY GAS
MOLE RATIO

FIGURE IV-A-2s

CONVERSION vs. CONTACT TIME

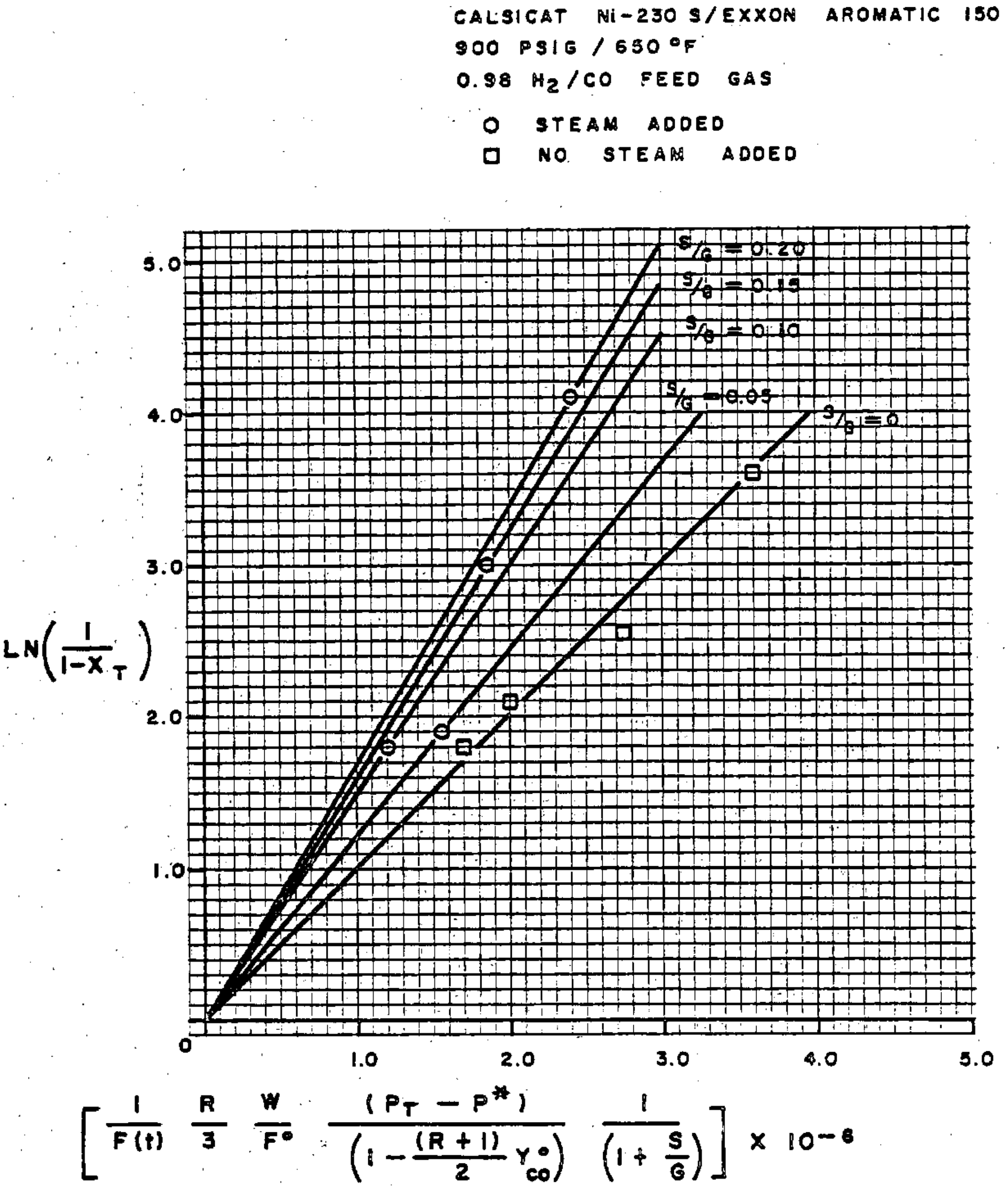


FIGURE IV–A–2 f

REACTION RATE CONSTANT
VS.
STEAM / GAS MOLE RATIO

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

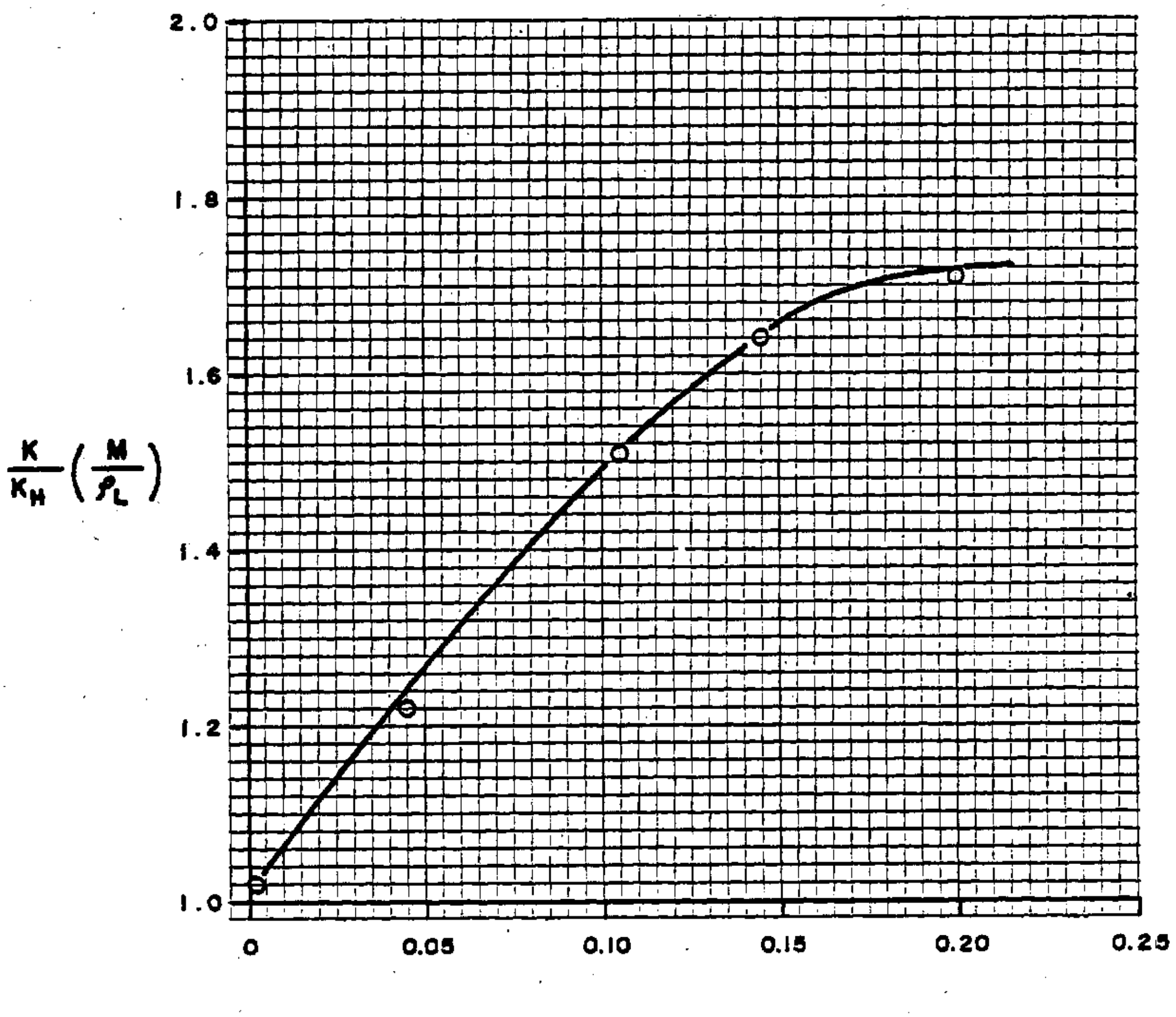


Table IV-A-3a

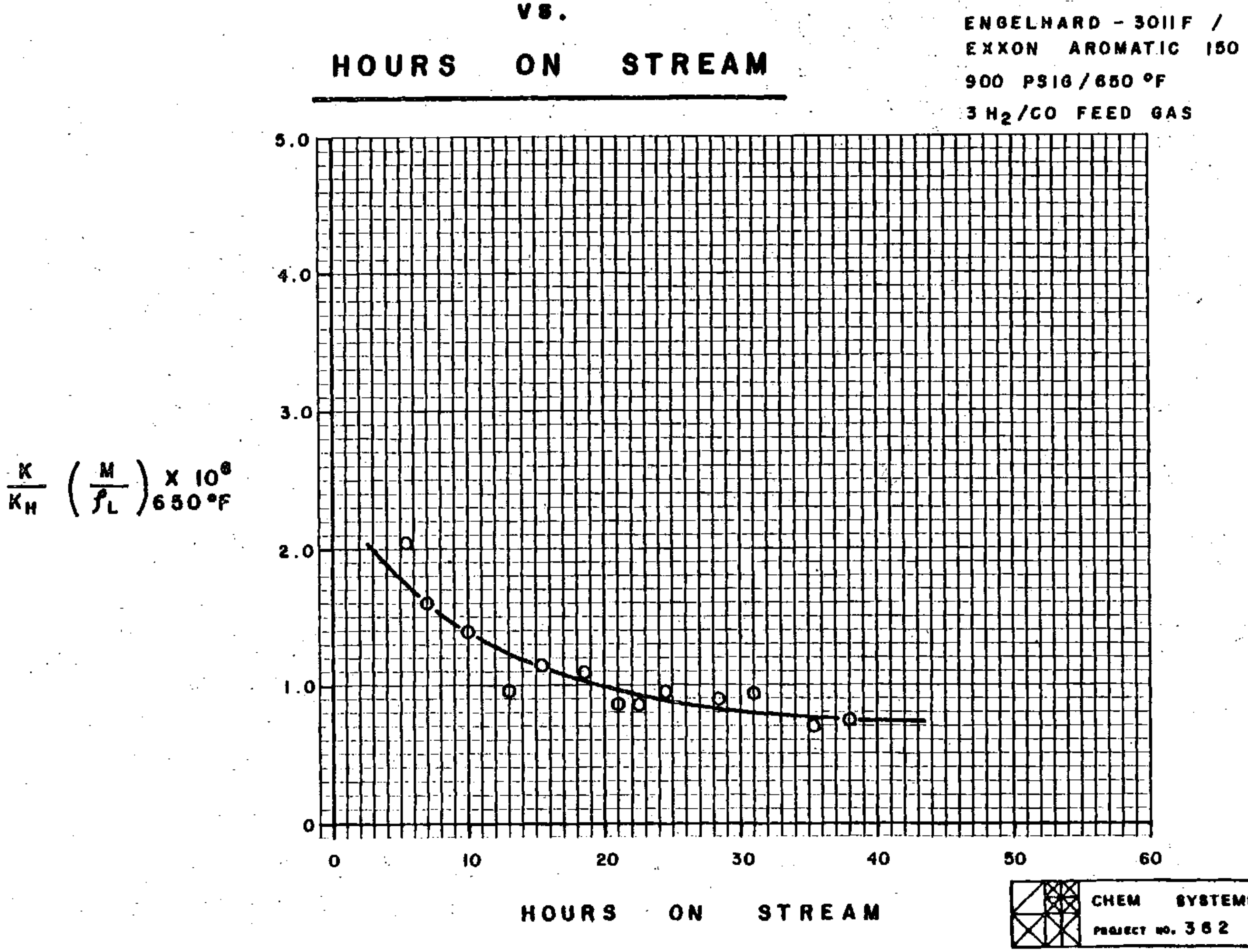
Process Variable Scan(1) - Engelhard 3011F(2)/Exxon Aromatic 150

Run No.	Temp. °F	VHSV Hr^{-1}	$\frac{K \times 10^6}{K_H(M/\rho_L)}_{650°}$	CO Conv. Percent	Feed H_2/CO	Effluent H_2/CO
1	651	4900	2.04	98.8	3/1	-
2A	651	5100	1.62	96.0	3/1	12.8
2B	651	6590	1.47	88.7	3/1	4.8
2C	654	5850	0.92	81.1	3/1	4.7
3A	651	4275	1.16	93.7	3/1	8.7
3B	651	5735	1.15	86.9	3/1	5.1
4A	651	4480	0.86	85.2	3/1	4.3
4B	651	5435	0.89	79.7	3/1	3.9
4C	650	6940	1.01	73.6	3/1	4.1
5A	651	4335	0.89	87.2	3/1	5.7
5B	651	5935	0.94	79.2	3/1	4.5
6A	651	3220	0.69	87.9	3/1	5.7
6B	651	4195	0.76	83.0	3/1	5.1

(1) Pressure = 900 psig, Feed Gas Composition = 75% H_2, 25% CO

(2) Catalyst Loading = 200 cm^3 = 243.5 gm

FIGURE IV-A-3a
CATALYST ACTIVITY
VS.
HOURS ON STREAM



CHEM SYSTEMS INC.
PROJECT NO. 362 DATE