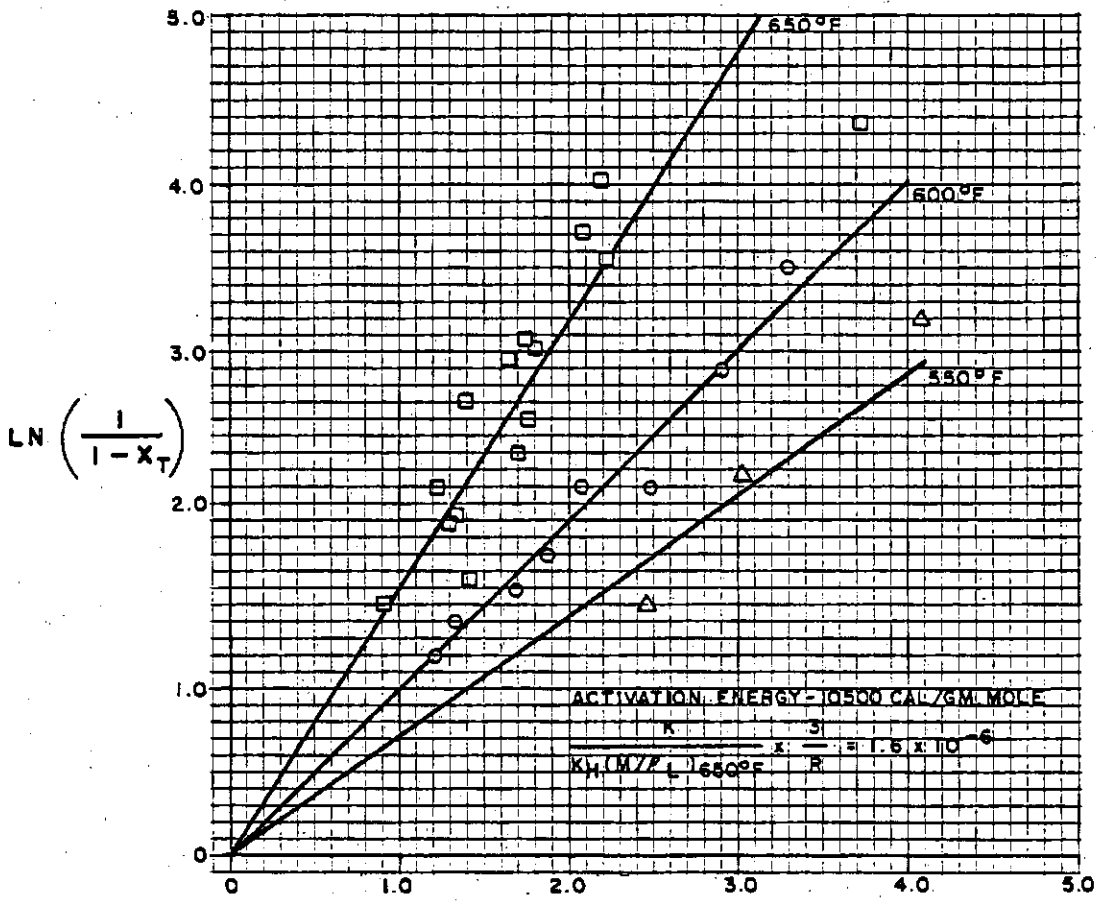
FIGURE IV-D-1c

CONVERSION VS. "CONTACT TIME"

PROCESS DEVELOPMENT UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
500-900 PSIG / 650°F $2H_2/1CO$ FEED GAS



$$RW(P_T - P^R)/3F^{\circ}F(t)\left[1 - \frac{(R+1)}{2}Y^{\circ}_{CO}\right] \times 10^{-6}$$

(Equation 1) for the three temperature levels investigated; 550°F, 600°F and 650°F. As can be seen from Figure IV-D-1c, straight lines were obtained indicating good agreement with the kinetic model. The scopes of the lines are the values of the reaction rate constants at the three temperature levels. Figure IV-D-1d shows these values plotted in an Arrhenius type plot. From this the activation energy was calculated at 10,500 cal/gm. mole. This is in excellent agreement with previous PDU results on the methanation reaction alone. In those earlier runs, activation energies of 9,000 to 11,000 cal./gm mole were obtained.

Figure IV-D-1e shows the PDU effluent gas H_2/CO molar ratio as a function of CO conversion. These ratios were approximately 20 to 30 percent higher than the H_2/CO ratios obtained in comparable bench scale runs. They are more than satisfactory as an acceptable feed to a downstream polishing reactor.

Throughout the entire duration of this process variable scan, no make-up process oil had to be added to the system. This proved out the effectiveness of the demister system added to the PDU and indicated that the excessive oil make-up rates, experienced with previous PDU runs, were not due to either chemical or thermal degradation of the process oil.

2. Calsicat Ni-230S/Witco 40 Mineral oil Reaction Rate Studies w/1.5 H_2/1CO Feed Gas

During March, a second process variable scan was initiated with the Calsicat Ni-230S/Witco 40 mineral oil system for the combined shift/methanation reaction using a 1.5 H_2/1CO feed gas. The first attempt at operating the PDU with the 1.5 H_2/1CO feed gas was aborted due to an oil leak in the reactor lower Grayloc seal ring. All attempts to fix the leak were unsuccessful and the reactor had to be unloaded. A second loading of catalyst was charged but was lost due to a malfunction in the temperature controller during the reduction procedure.

FIGURE IV-D-1d

KINETIC RATE CONSTANT VS. TEMPERATURE

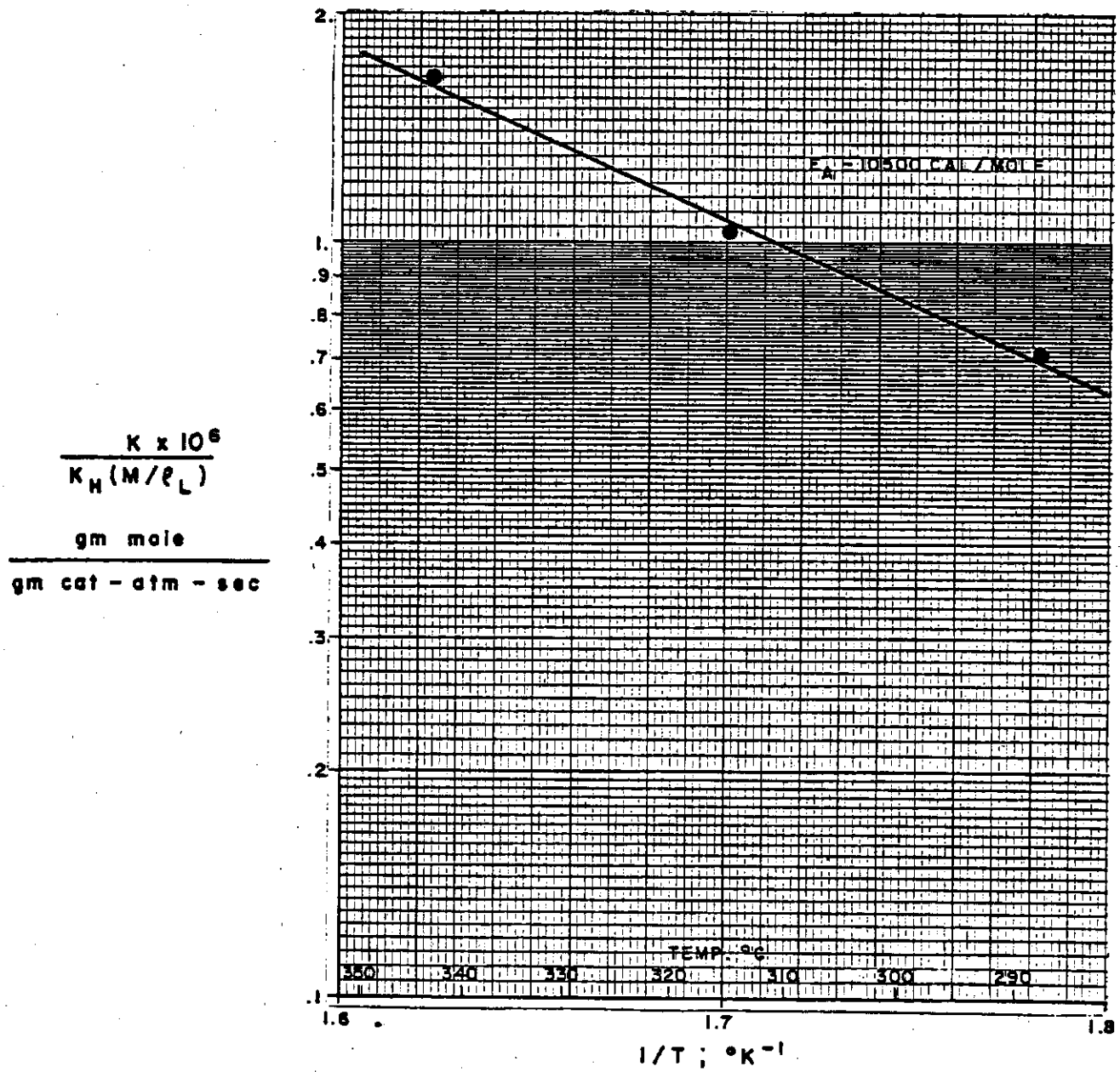
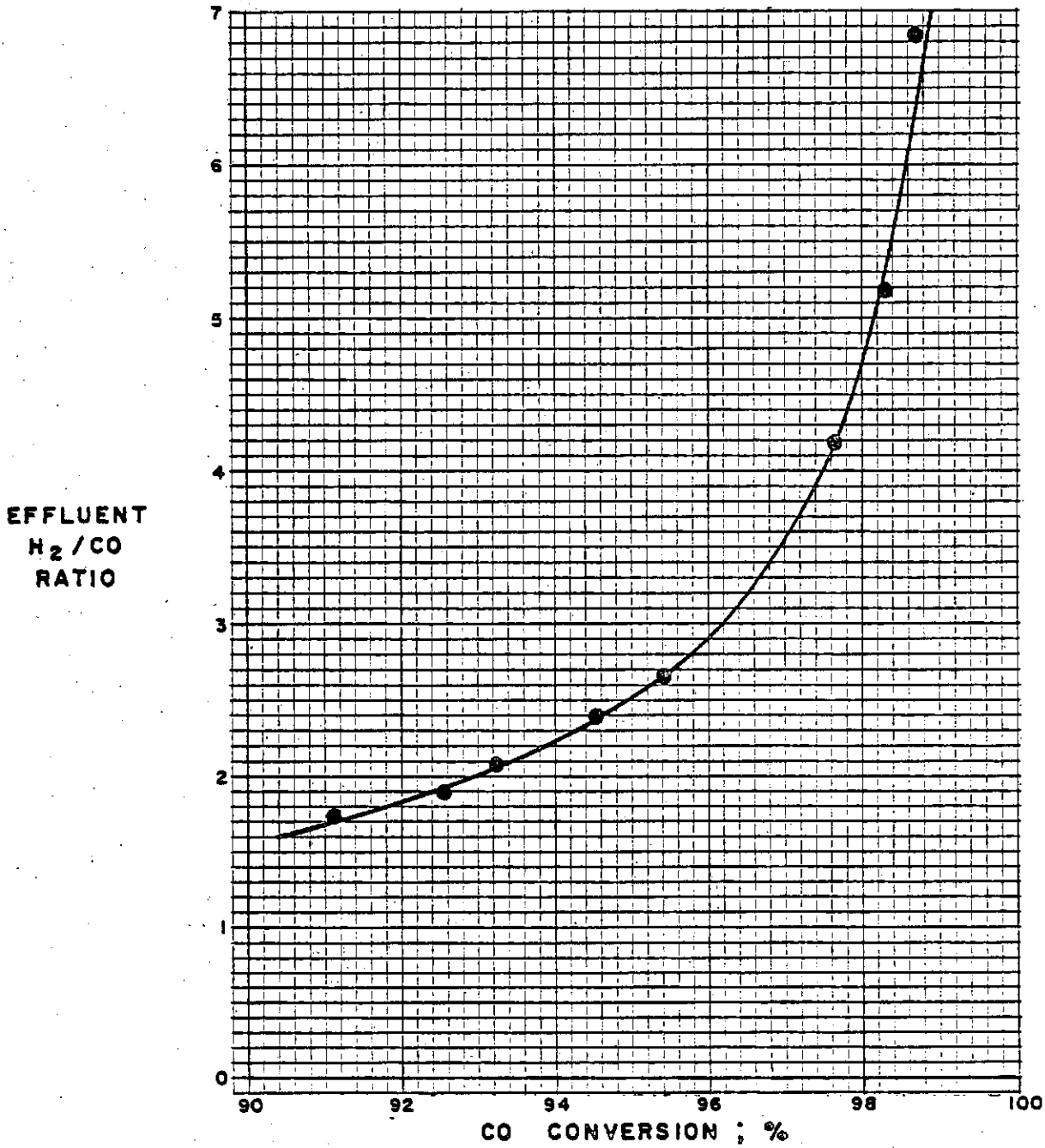


FIGURE IV-D-1e

EFFLUENT H_2/CO RATIO VS. CONVERSION

PROCESS DEVELOPMENT UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
900 PSIG / 650°F $2H_2/1CO$ FEED GAS



The third catalyst loading was successfully put on-stream and the results of the complete process variable scan are indicated in Table IV-D-2a. All of the runs were performed at a pressure of 500 psig and a nominal reaction temperature of 650°F. Inlet gas flow rates were varied to measure catalyst performance. Figure IV-D-2a show catalyst activity as a function of on-stream time. After 40 hours on-stream, the activity appeared to stabilize at a level equivalent to a reaction rate constant of 2.1×10^{-6} gm. mole/gm. cat.-atm.-sec. at 650°F. This is about 20 percent higher than the value obtained with the previous batch of Calsicat catalyst and the $2H_2/1CO$ feed gas. This high value is believed to be more representative of the system productivity, since the feed and effluent flow measuring devices had been recalibrated just prior to initiating the variable scan.

Figure IV-D-2b shows the catalyst activity factor used to correlate the results. Figure IV-D-2c is a plot of conversion versus "contact time" as developed by the kinetic model. Again, it can be seen that the data fit the kinetic expression. Figure IV-D-2d shows the effluent gas H_2/CO molar ratio as a function of CO conversion. The values are similar to those obtained in the bench scale unit with the same feed gas. Based on polishing reactor studies, this effluent gas could be fed to a polishing reactor with a small quantity of additional steam approximately 10 percent of the dry gas feed, and complete CO conversion would be effected.

3. Calsicat Ni-230S/Witco 40 Mineral Oil Reaction Rate Studies w/1.4 $H_2/1CO$ Feed Gas

During the month of April, 1976, a process variable scan was initiated with the Calsicat Ni-230S (reduced and stabilized)/Witco 40 Mineral Oil system to study the combined shift/methanation reaction with a 1.4/1 H_2/CO feed gas molar ratio. Of particular concern was the effect of direct steam addition on reaction rate and product gas composition. The reduced and stabilized version of the catalyst, as opposed to the

Table IV-D-2a

PDU Process Variable Scan

Calsicat Ni-230S*/Witco 40 Mineral Oil

Run No.	Temp. °F	Pressure psig	VHSV Hr^{-1}	CO Conv. %	$\frac{K \times 10^6}{K_H(M/\rho_L)_{650^oF}}$	$\frac{K \times 10^6}{K_H(M/\rho_L)_{650^oF}} \times \frac{3}{R}$	Effluent H_2/CO Ratio
2-1	651	500	2525	99.7	2.62	5.69	10.07
2-2	650	500	2455	99.6	2.24	4.86	9.45
2-3	649	500	2620	98.6	1.98	3.96	2.6
2-4	652	500	4895	87.8	1.78	3.56	0.51
2-5	648	500	2485	97.7	1.63	3.26	1.69
2-6	647	500	2310	94.8	1.23	2.46	0.87
2-7	647	500	3900	85.9	1.37	2.74	0.45
2-8	651	500	2095	93.8	1.01	2.02	0.71
2-9	650	500	2965	88.0	1.10	2.20	0.49
2-10	654	500	5110	78.3	1.33	2.66	0.43
2-11	650	500	4095	82.3	1.24	2.48	0.45
2-12	650	500	2250	93.2	1.05	2.10	0.66
2-13	647	500	3390	82.0	1.02	2.04	0.407

FIGURE IV-D-2a

CATALYST ACTIVITY VS. TIME

PROCESS DEVELOPMENT UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
500 PSIG / 650°F 1.5H_2/1 CO FEED GAS

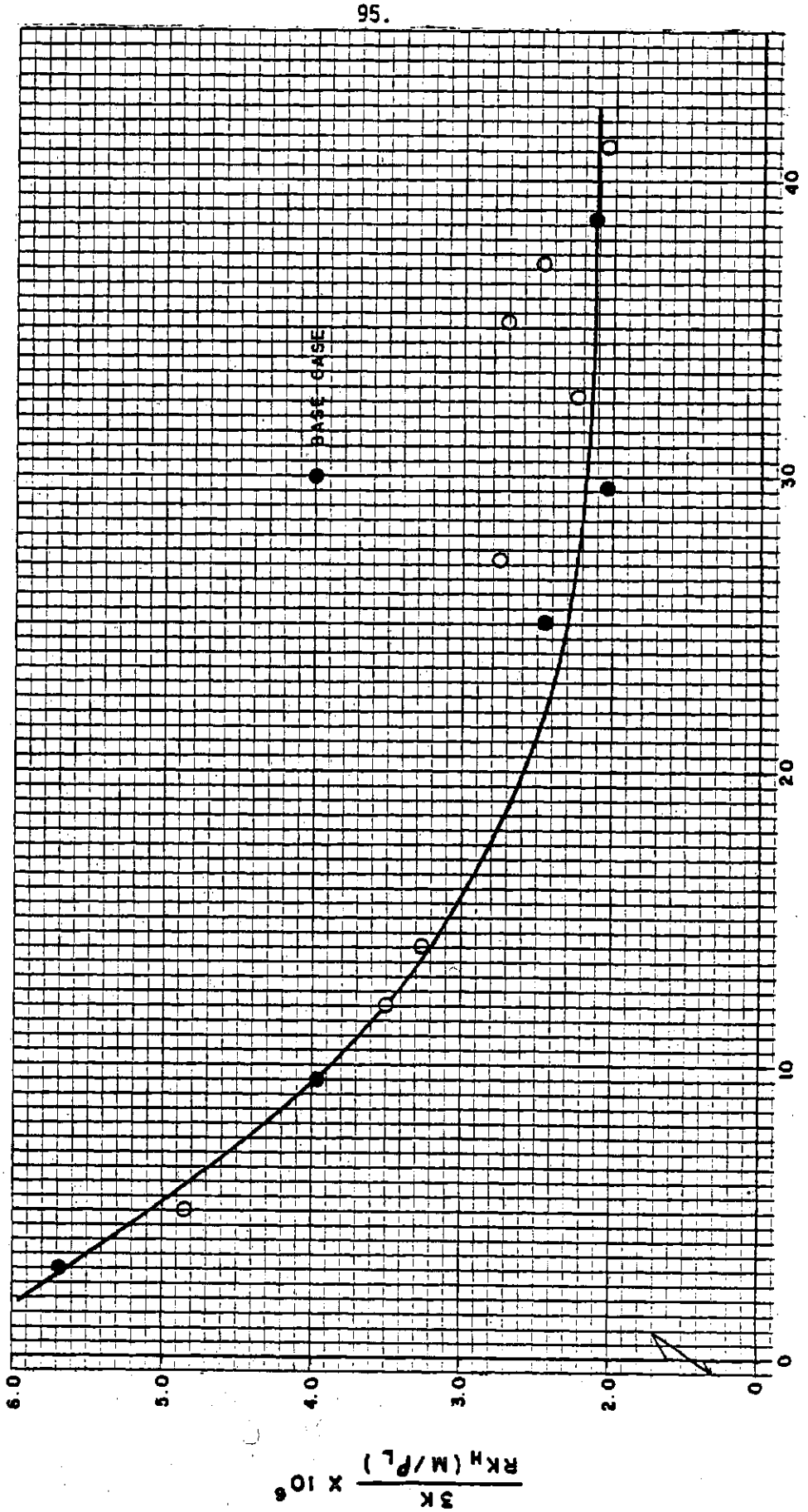


FIGURE IV-D-2b

ACTIVITY CORRECTION FACTOR VS. HOURS ON STREAM

PROCESS DEVELOPMENT UNIT
CALISCAT NI-2303 / WITCO 40 MINERAL OIL
500 PSIG / 650°F 1.5 H_2 / ICO FEED GAS

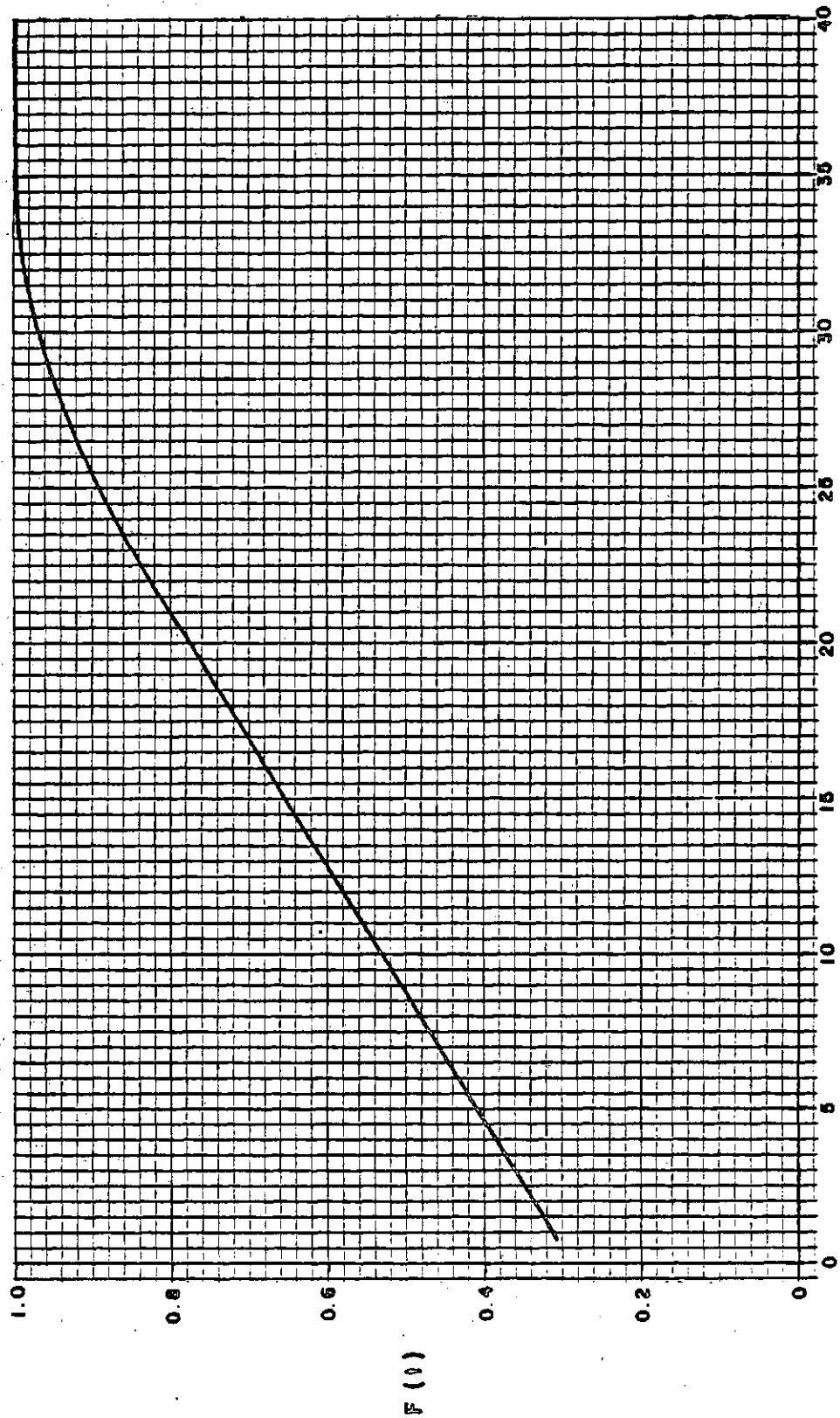
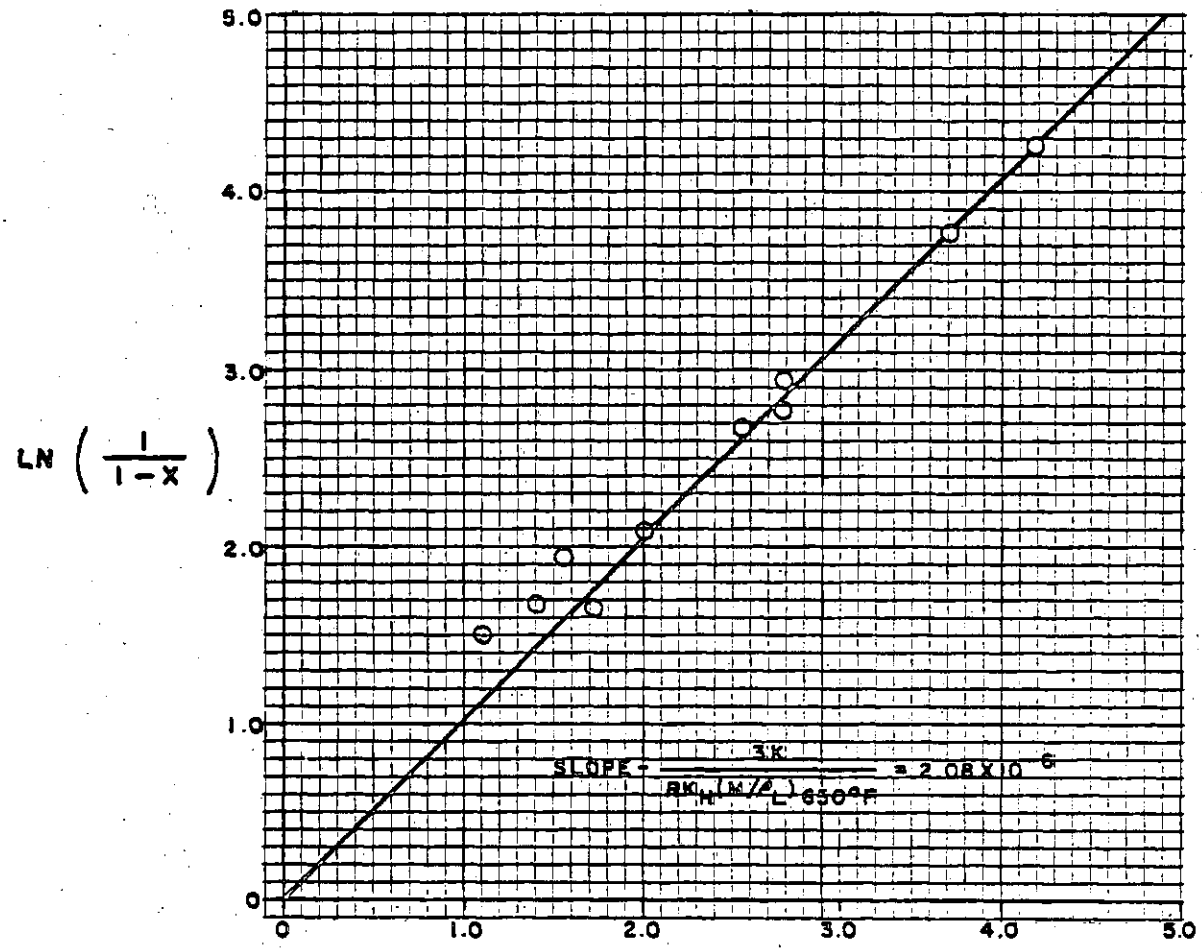


FIGURE IV-D-2c

CONVERSION VS. "CONTACT TIME"

PROCESS DEVELOPMENT UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
500 PSIG / 650°F 1.5 H_2 / 1 CO FEED GAS

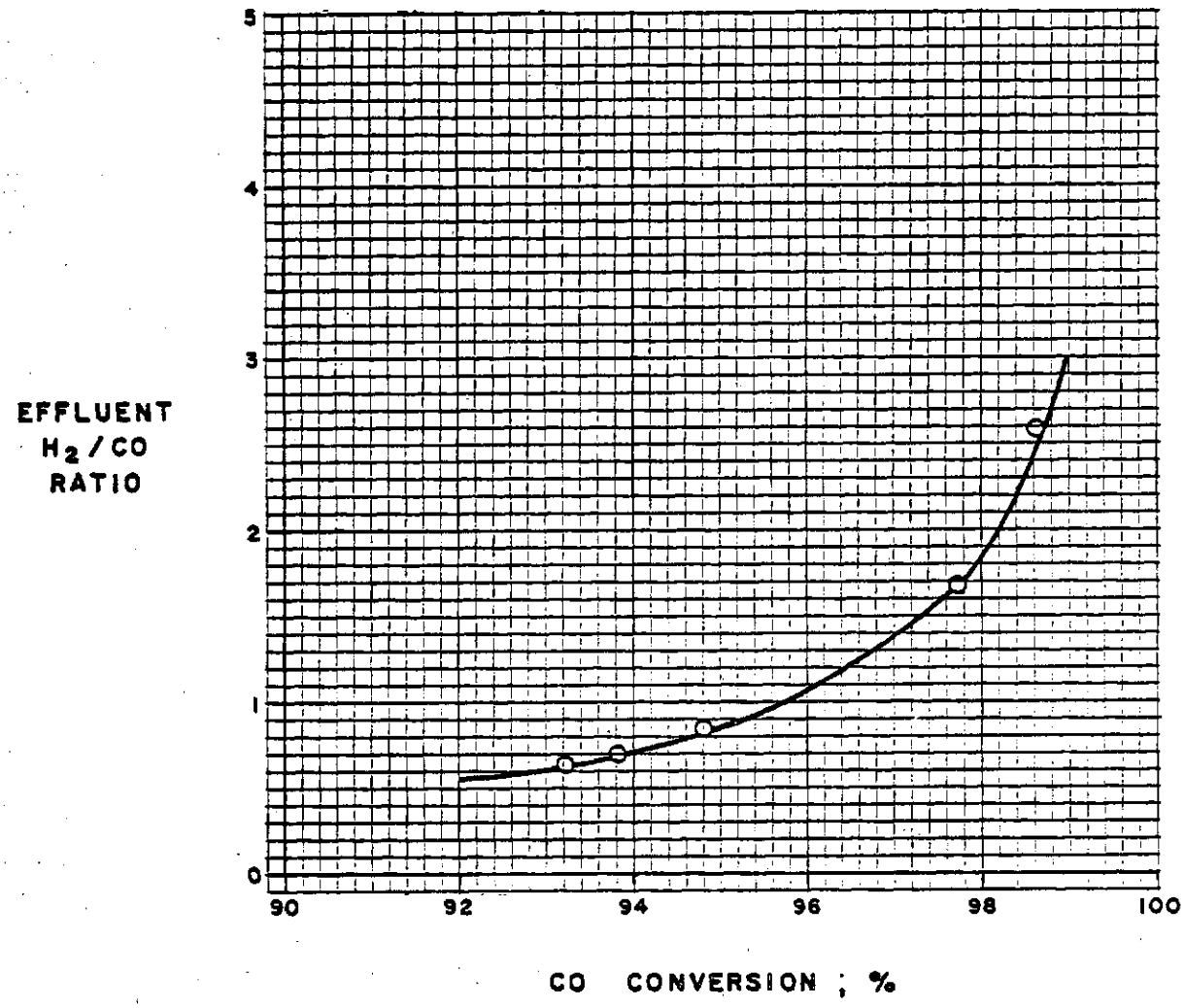


$$RW(P_T - P^n) / 3F°F(1) \left[1 - \frac{(R+1)}{2} Y°_{CO}\right] \times 10^{-6}$$

FIGURE IV-D-2d

EFFLUENT H_2/CO RATIO VS. CONVERSION

PROCESS DEVELOPMENT UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
500 PSIG / 650°F 1.5H_2 / 1 CO FEED GAS



to the previously used oxide form, was chosen to reduce the time required to put this system on-stream. This was done to make up for a short delay resulting from a mechanical seal failure in the process oil circulating pump.

The results for the process variable scan are presented in Table IV-D-3a. Figure IV-D-3a shows the catalyst activity as a function of hours on-stream. Figure IV-D-3b represents the activity correction factor used to plot data according to the reaction rate model (Equation 1).

Figure IV-D-3c indicates a plot of CO conversion versus "contact time" for these data.

Based on this model, at 650^{0}F, the slope of the conversion vs. contact time curve for a 1.4 H_2/1CO feed gas (without water addition) gives a value of 1.4 x 10^{-6} gm moles/gm cat-atm-sec for the reaction rate constant. This compares with values ranging from 1.8 x 10^{-6} gm mole/gm cat-atm-sec for work previously reported on the Bench Scale and Process Development units using the oxide form of the catalyst, which was reduced with H_2 in situ. The lower activity for this catalyst loading was probably a result of the inability of all the stabilized catalyst sites to revert to their active form while in the presence of the liquid phase. It is believed that had this catalyst been treated with H_2 prior to introducing the process oil, it would have displayed a normal activity level.

Figure IV-D-3d shows the effect of varying the molar steam to gas ratio. Only a minimal benefit in the reaction rate constant is obtained up to a steam to gas ratio of 0.3. Under the same conditions, the bench scale unit indicated a more pronounced increase in reactivity at about a 0.1 steam to gas ratio. Nevertheless, the most obvious effect of direct steam addition is on the effluent gas H_2/CO ratio, which is an important consideration with respect to operation of the downstream reactor in commercial operation. Figure IV-D-3e indicates that for

Table IV-D-3a

PDU Process Variable Scan*

Calsicat Ni-230**/Witco 40 Mineral Oil

1.4 H_2:1CO Feed Gas

Run No.	Temp. °C	VHSV Hr^{-1}	CO Conv. Percent	Effluent H_2/CO Ratio	Molar Steam/ Dry Gas Ratio	$\frac{k \times 10^6}{K_H (M/\rho_L)_{650^oF}} \times \frac{3}{R}$
3-1	646	1950	98.8	3.74	-	3.14
3-2	658	1975	98.7	3.51	-	2.77
3-3	656	2025	97.6	2.42	-	2.44
3-4	651	2030	96.1	1.44	-	2.37
3-5	653	2020	96.6	2.37	0.06	2.34
3-6	650	2200	96.4	3.21	0.13	2.46
3-7	650	2230	91.0	0.60	-	1.95
3-8	649	2190	92.7	1.93	0.18	2.09
3-9	647	2170	92.4	2.17	0.23	2.06
3-10	650	2195	92.6	NA	0.29	1.96
3-11	643	1950	87.3	0.44	0.06	1.76
3-12	655	1690	94.6	1.50	0.08	1.87
3-13	655	1730	93.5	1.65	0.15	1.71
3-14	654	2145	85.5	0.45	-	1.45
3-15	650	1920	86.7	1.18	0.18	1.64
3-16	650	1945	91	1.75	0.18	1.53
3-17	652	1930	89.3	1.30	0.14	1.43
3-18	653	2380	86.9	0.48	-	1.50
3-19	655	2335	87.2	0.93	0.10	1.44
3-20	652	1915	90	1.29	0.12	1.58
3-21	653	2030	88	1.08	0.10	1.48

*500 psig

**Reduced and stabilized formulation

FIGURE IV-D-3 e

CATALYST ACTIVITY VS. TIME

PROCESS DEVELOPMENT UNIT

CALSICAT Ni-230 REDUCED + STABILIZED

WITCO 40 MINERAL OIL

500 PSIG / 630 °F

1.4 H_2 / CO FEED GAS

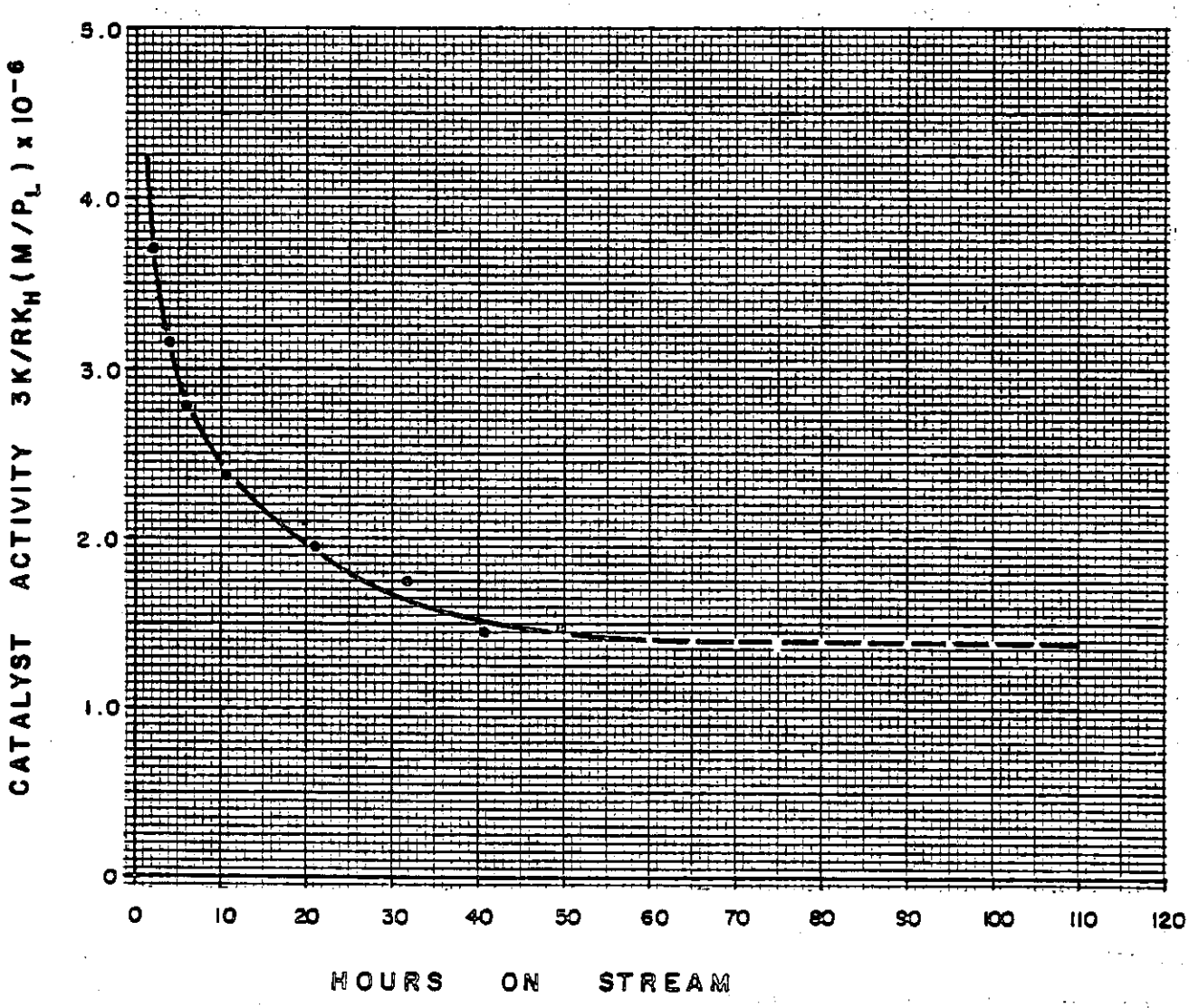


FIGURE IV-D-3b

ACTIVITY CORRECTION FACTOR VS. HOURS ON STREAM

PROCESS DEVELOPMENT UNIT
CALSICAT Ni-230 REDUCED + STABILIZED
WITCO 40 MINERAL OIL
500 PSIG / 650 °F
1.4 H_2/CO FEED GAS

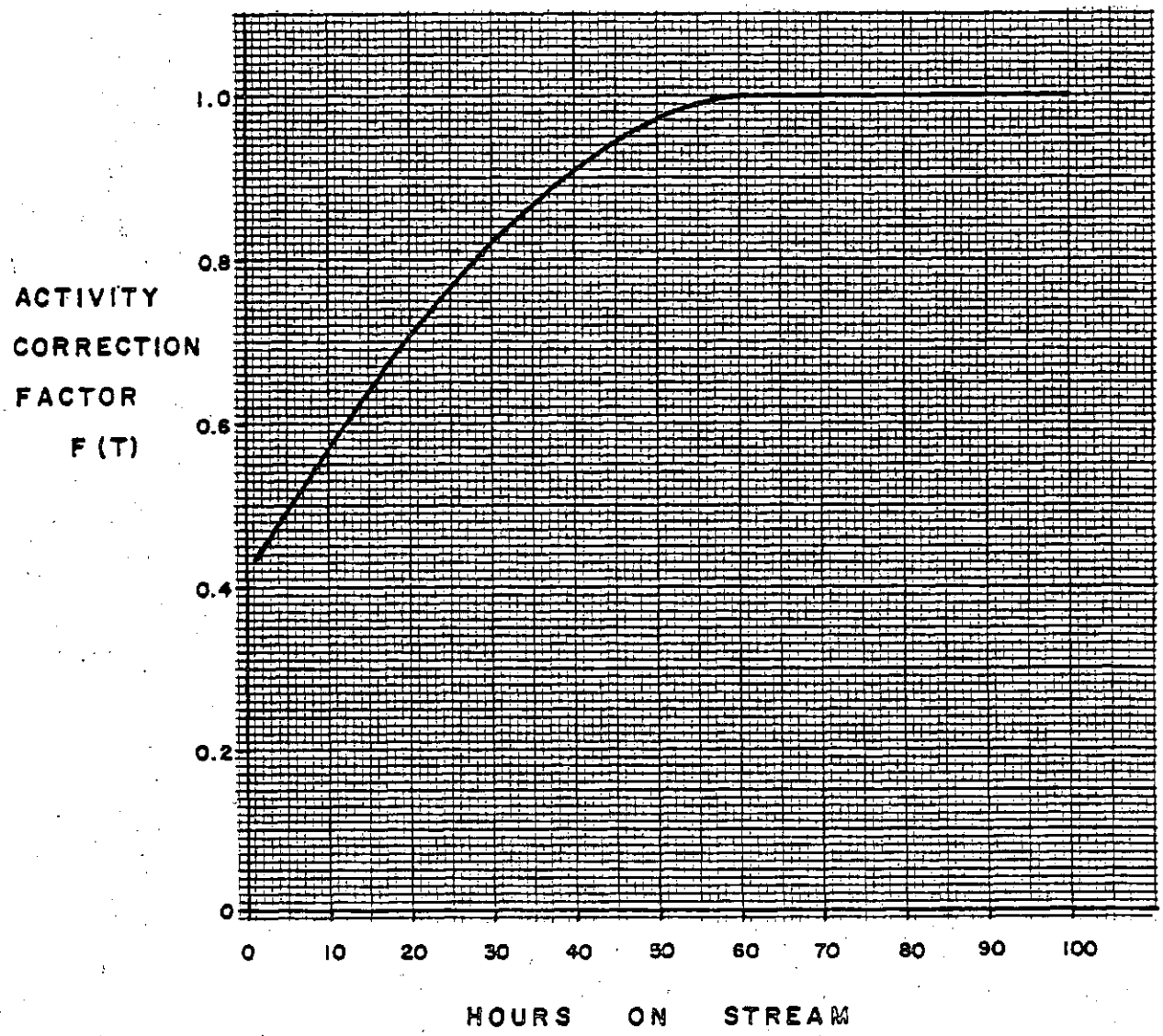


FIGURE IV-D-3c

CONVERSION VS. CONTACT TIME

PROCESS DEVELOPMENT UNIT
CALSICAT Ni-230 REDUCED + STABILIZED
WITCO 40 MINERAL OIL
500 PSIG / 650 °F
1.4 H_2/CO FEED GAS

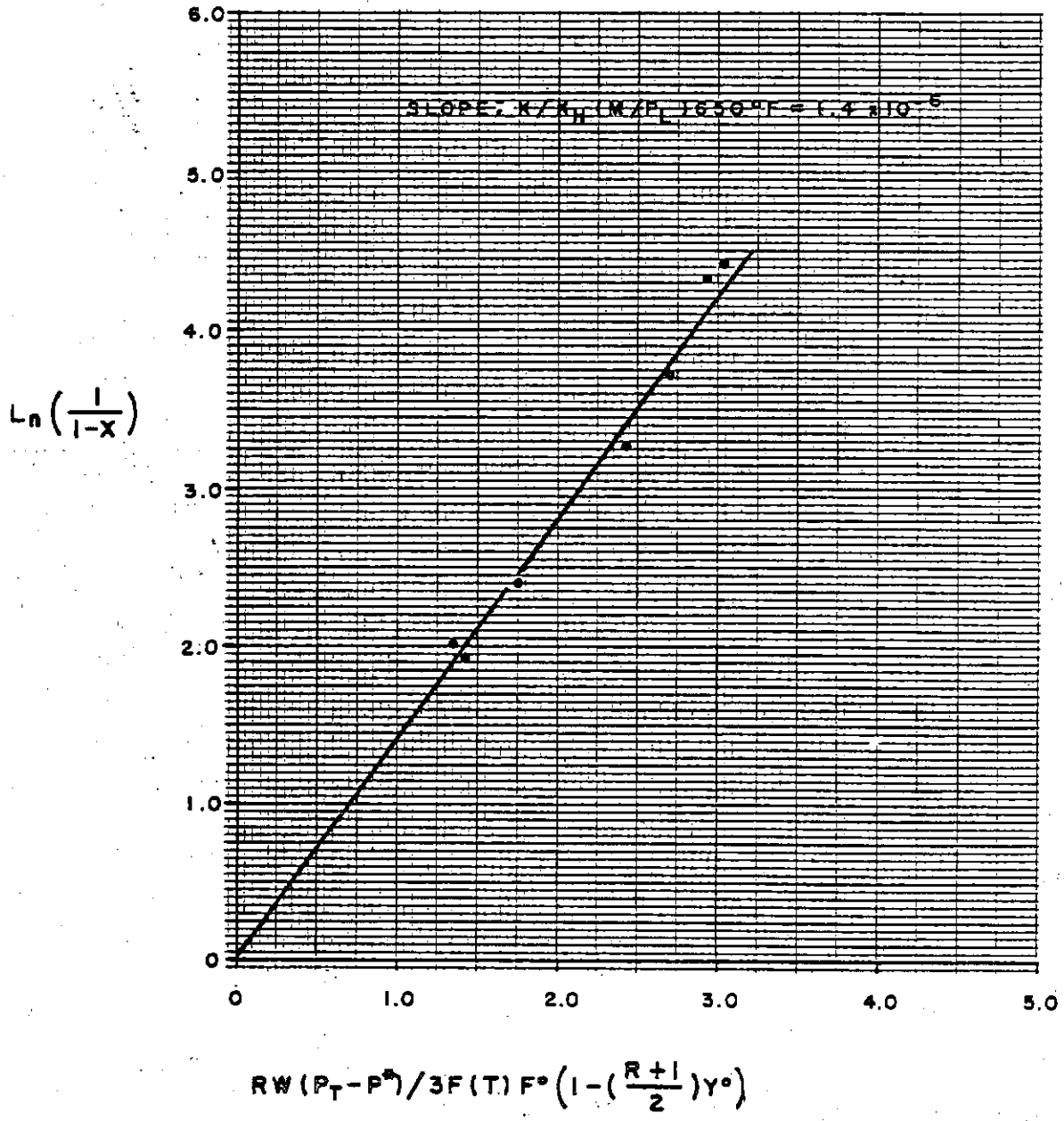


FIGURE IV-D-3d

REACTION RATE CONSTANT VS. STEAM TO GAS RATIO

PROCESS DEVELOPMENT UNIT
CALSICAT Ni-230 REDUCED + STABILIZED
WITCO 40 MINERAL OIL
500 PSIG / 650°F
1.4 H_2/CO FEED GAS

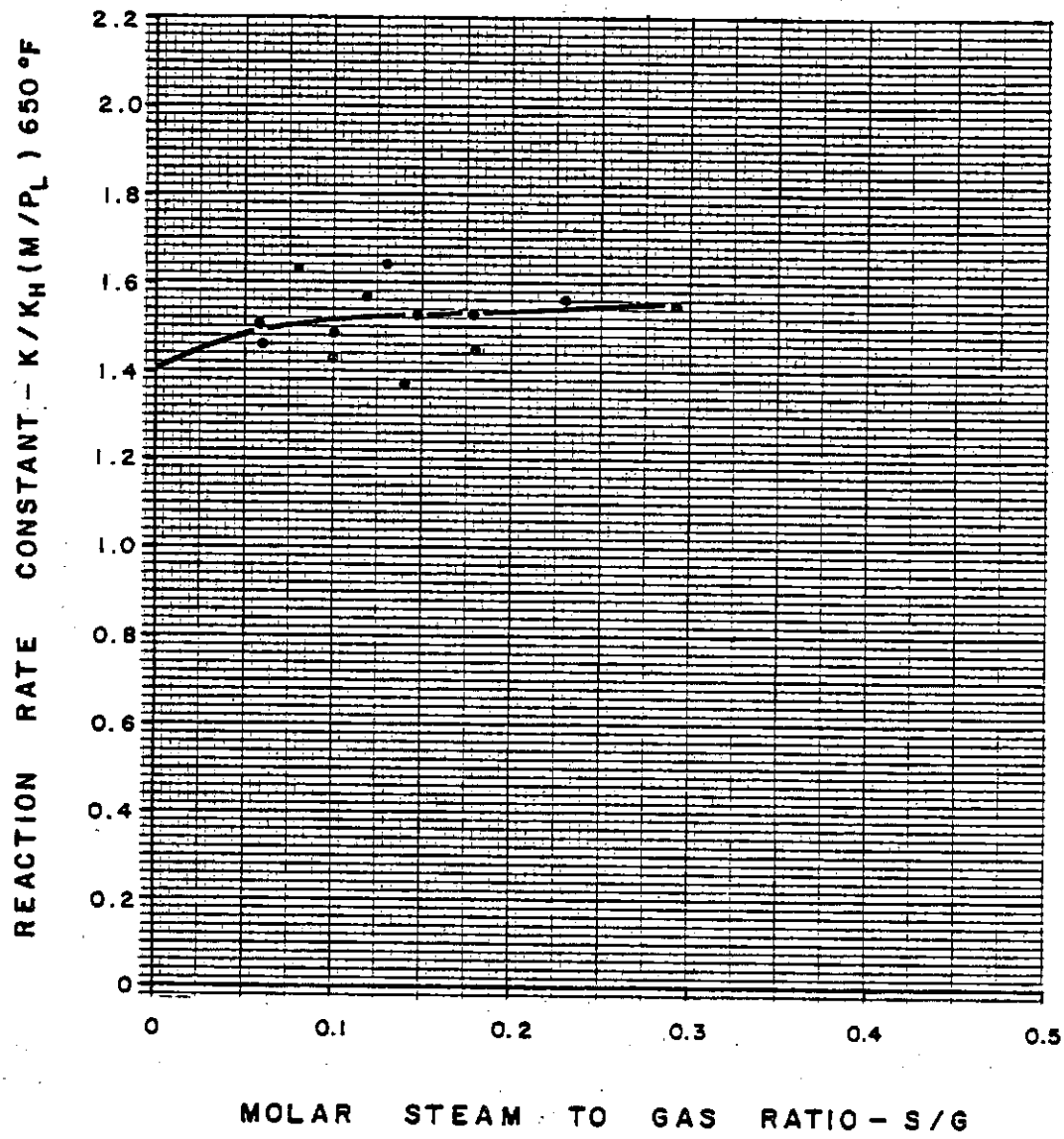
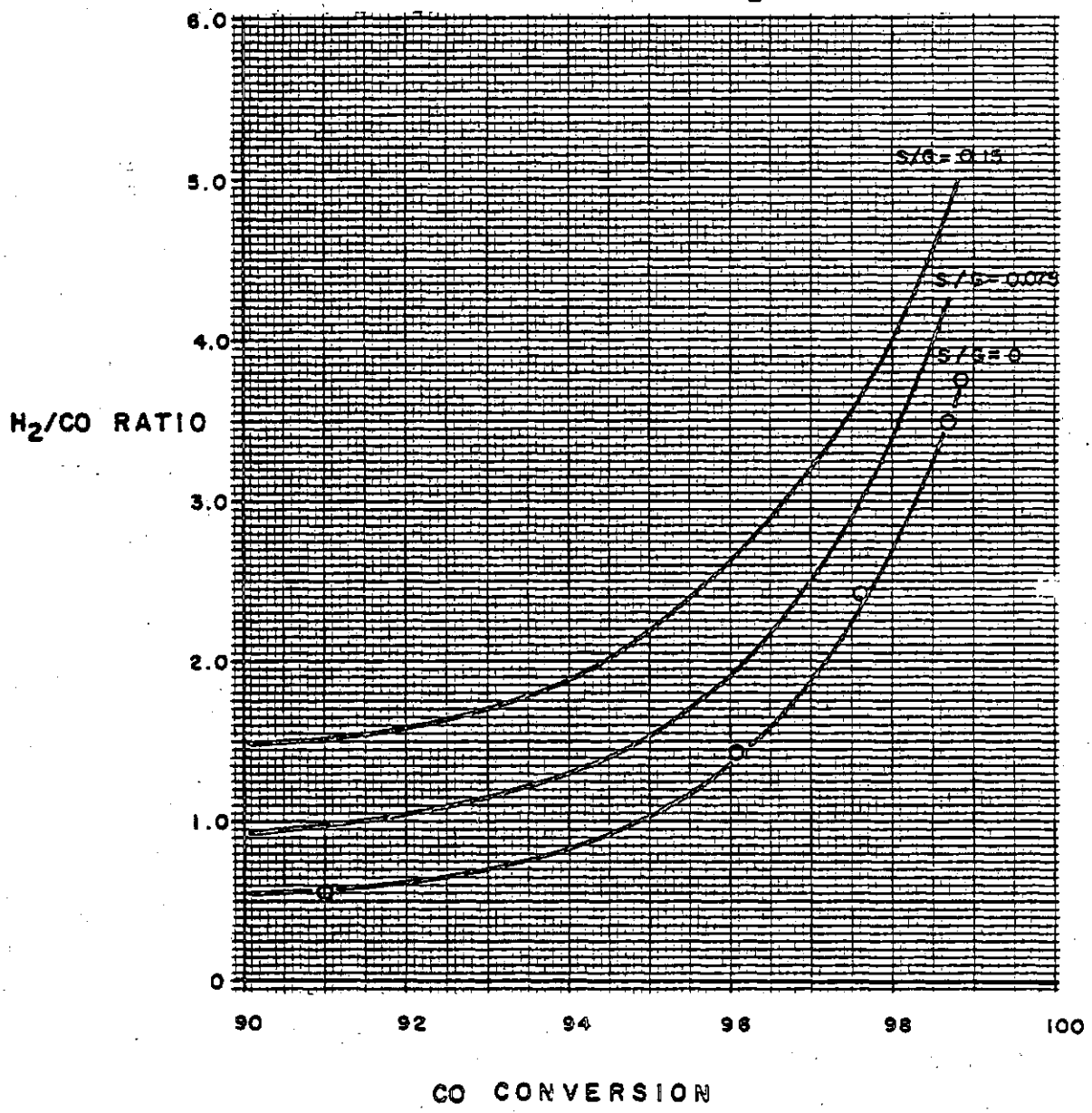


FIGURE IV-D-3e

EFFLUENT H_2/CO RATIO VS. CONVERSION

PROCESS DEVELOPMENT UNIT
CALSICAT Ni-230 REDUCED + STABILIZED
WITCO 40 MINERAL OIL
500 PSIG/650°F, 1.4 H_2/CO FEED GAS



the 1.4 H_2/1CO feed gas, almost no additional steam is necessary to obtain an effluent gas H_2/CO ratio of equal to or greater than 2 at a conversion level of 97-98 percent. This was an improvement over the bench scale results, which indicated that about 0.05-0.10 moles of steam per mole of feed gas would be required to insure the necessary effluent gas H_2/CO ratio.

4. Calsicat Ni-230S/Witco 40 Mineral Oil Reaction Rate Studies w/1.02 H_2/1CO Feed Gas

Utilizing the same catalyst charge as in Section IV-D-3 above, the feed gas was switched to a 1.02 H_2/CO ratio and runs continued to investigate the effect of direct steam injection. The results for this variable scan are presented in Table IV-D-4a and shown graphically in Figures IV-D-4a and b. As with the 1.4 H_2/1CO feed gas, the addition of steam resulted in a nominal increase in the reaction rate constant up to 0.3-0.4 moles of steam per mole of feed gas. Since there is an economic penalty for steam use, the level of steam is really determined by the amount necessary to result in an effluent gas H_2/CO ratio satisfactory for use in the polishing reactor. As Figure IV-D-4b indicates, this is about 0.15-0.20 moles of steam per mole of feed gas which is in excellent agreement with the recent bench scale results on the same synthesis gas feed. This is still significantly less than what is required by a separate shift-conversion unit followed by a methanation unit operating on a balanced 3/1 H_2/CO feed gas. However, since the catalyst required for the LPM/S reactor is roughly inversely proportional to the feed gas H_2/CO ratio, it is more economical to shift the H_2/CO ratio to some intermediate level prior to reaction in the LPM/S reactor. This is covered in considerable detail in the process evaluation study, Section IV-F.

With the completion of this process variable scan, the experimental program for the combined shift/methanation reaction in the PDU was

Table IV-D-4a

PDU Process Variable Scan*
Calsicat Ni-230**/Witco 40 Mineral Oil
1.02 H_2:1CO Feed Gas

Run No.	Temp. °C	VHSV Hr^{-1}	CO Conv. Percent	Effluent H_2/CO Ratio	Molar Steam/ Dry Gas Ratio	$\frac{k \times 10^6}{K_H (M/\rho_L)_{650°F}} \times \frac{3}{R}$
3-22	646	1355	80	0.43	0.165	1.15
3-23	645	1475	80.3	0.56	0.209	1.27
3-24	648	1475	78.8	0.31	0.094	1.18
3-25	652	1110	90	1.03	0.197	1.27
3-26	650	955	95.4	3.85	0.426	1.48
3-27	650	945	95.1	4.42	0.508	1.46
3-28	650	835	95.3	3.4	0.347	1.30
3-29	647	875	95.4	4.99	0.547	1.25
3-30	650	865	92.6	1.16	0.155	1.13
3-31	650	830	96.4	4.09	0.371	1.40
3-32	647	860	95.5	4.56	0.585	1.38
3-33	650	890	94.75	2.63	0.285	1.32
3-34	649	900	93.7	2.78	0.394	1.25

*500 psig

**Reduced and stabilized formulation

FIGURE IV-D-4a

REACTION RATE CONSTANT VS. STEAM TO GAS RATIO

PROCESS DEVELOPMENT UNIT
CALSICAT Ni-230 REDUCED + STABILIZED
WITCO 40 MINERAL OIL
500 PSIG/650 °F
1.02 H_2/CO FEED GAS