Figure IV-A-3b shows a plot of conversion versus "contact time" for this system. The reaction rate constant was calculated at 0.75×10^{-6} gm mole/gm cat.-atm-sec. This was too low, by a factor of 2-3, to be a viable catalyst candidate for the LPM process.

Table IV-A-3b summarizes the process variable scan on an Engelhard #4039Y (1/16" extrudates, 1/2 percent Rv on alumina) Witco 40 mineral oil system. At 650°F and 900 psig, the catalyst exhibited a low initial activity and a rapid decline in activity as a function of time on-stream. (See Figure IV-A-3c). The activity of this catalyst was an order of magnitude lower than the 3011F catalyst reported above. Due to the unsuitable activity characteristics of this catalyst, all work was terminated after thirty hours on-stream. Upon termination of the run, the bench scale reactor was cleaned and placed on standby.

FIGURE IV-A-3b

CONVERSION vs. CONTACT TIME

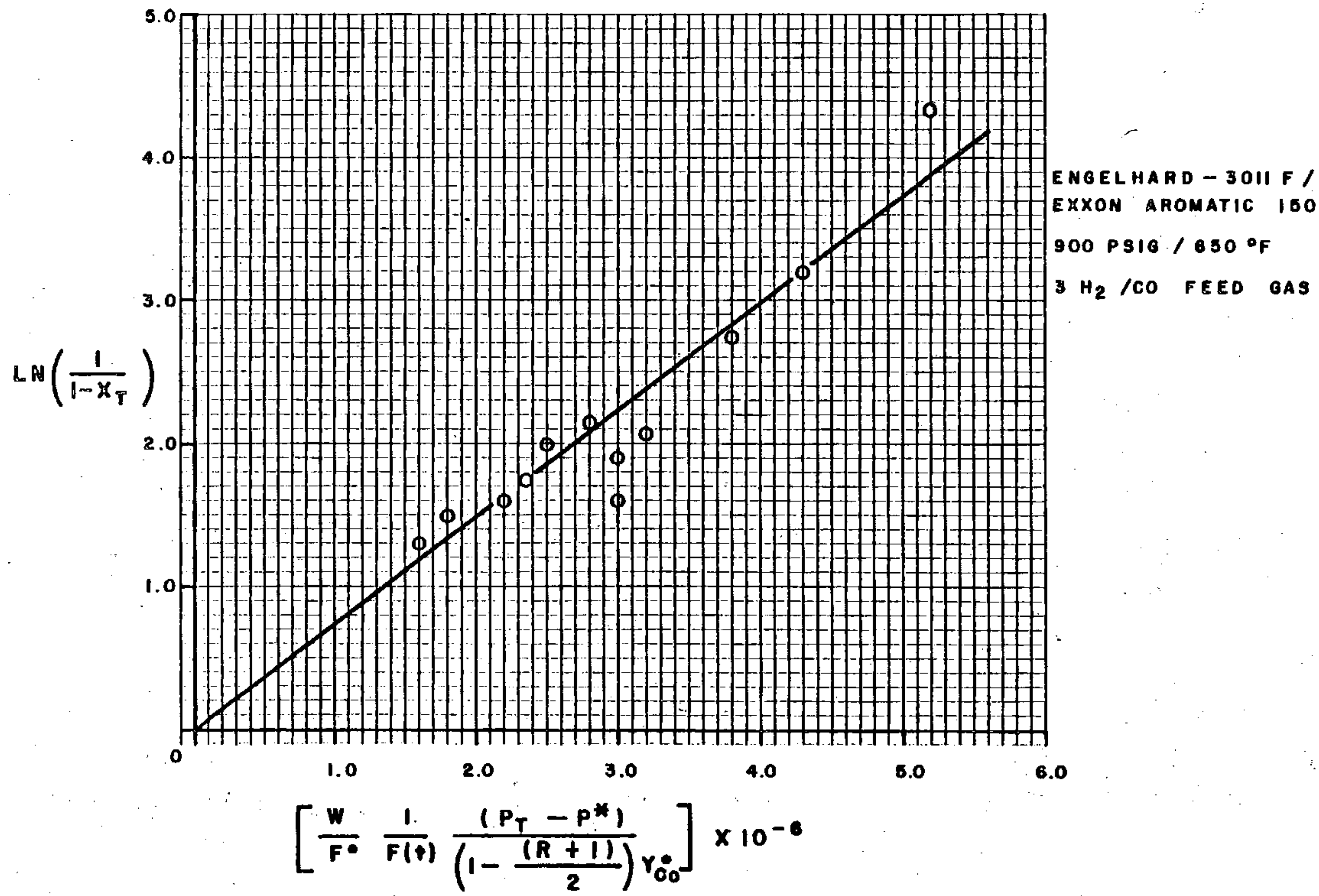


Table IV-A-3b

Process Variable Scan* - Engelhard 4039Y**/Witco 40

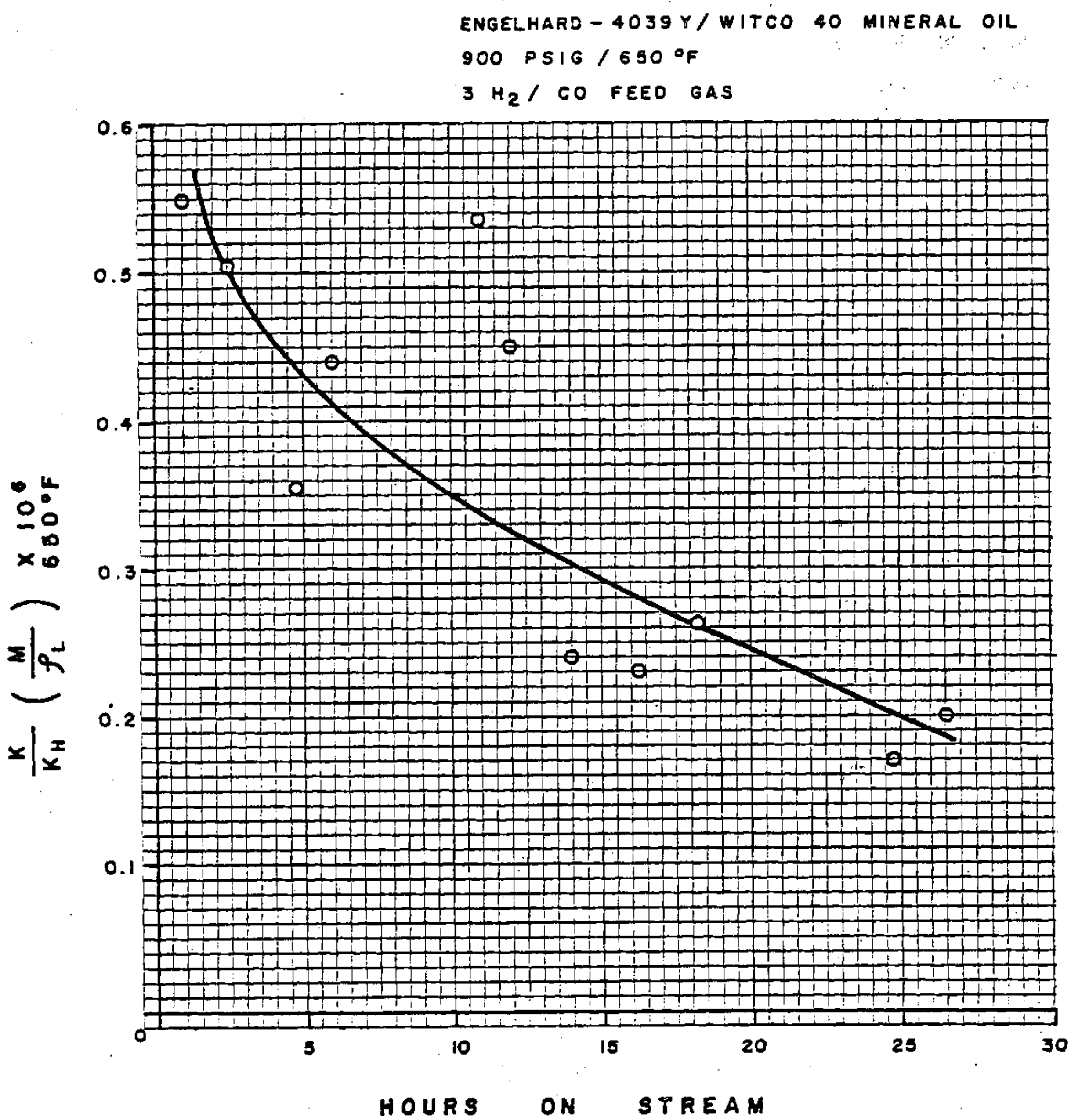
Run No.	Temp.	VHSV	CO Conversion	K/K_H $(M/\rho_L) \times 10^{-6}$ 650^oF
1A	651	1265	59.33	0.552
B	651	5055	57.40	0.504
C	651	4840	46.74	0.357
D	651	5665	48.75	0.442
2A	651	5375	57.63	0.538
B	651	5600	49.91	0.451
3A	651	5335	32.51	0.242
B	651	5335	31.29	0.231
C	651	5775	32.72	0.263
4A	651	5415	25.35	0.165
B	651	5545	27.06	0.201

*Pressure = 900 psig, Feed Gas Composition = 75% H_2, 25% CO

**Catalyst Loading = 150 cm^3 = 124.7 gm

FIGURE IV-A-3c

CATALYST ACTIVITY VS. HOURS ON STREAM



B. Life Unit

The life test was prematurely terminated due to a ruptured line in the feed oil system after 1400 hours on-stream. The cause of the line rupture was determined to be a plug in the reactor resulting when the temperature controller failed in the energized state causing the reactor temperature to go over 500°C. The temperature controller was returned to Electronic Control Systems and repaired.

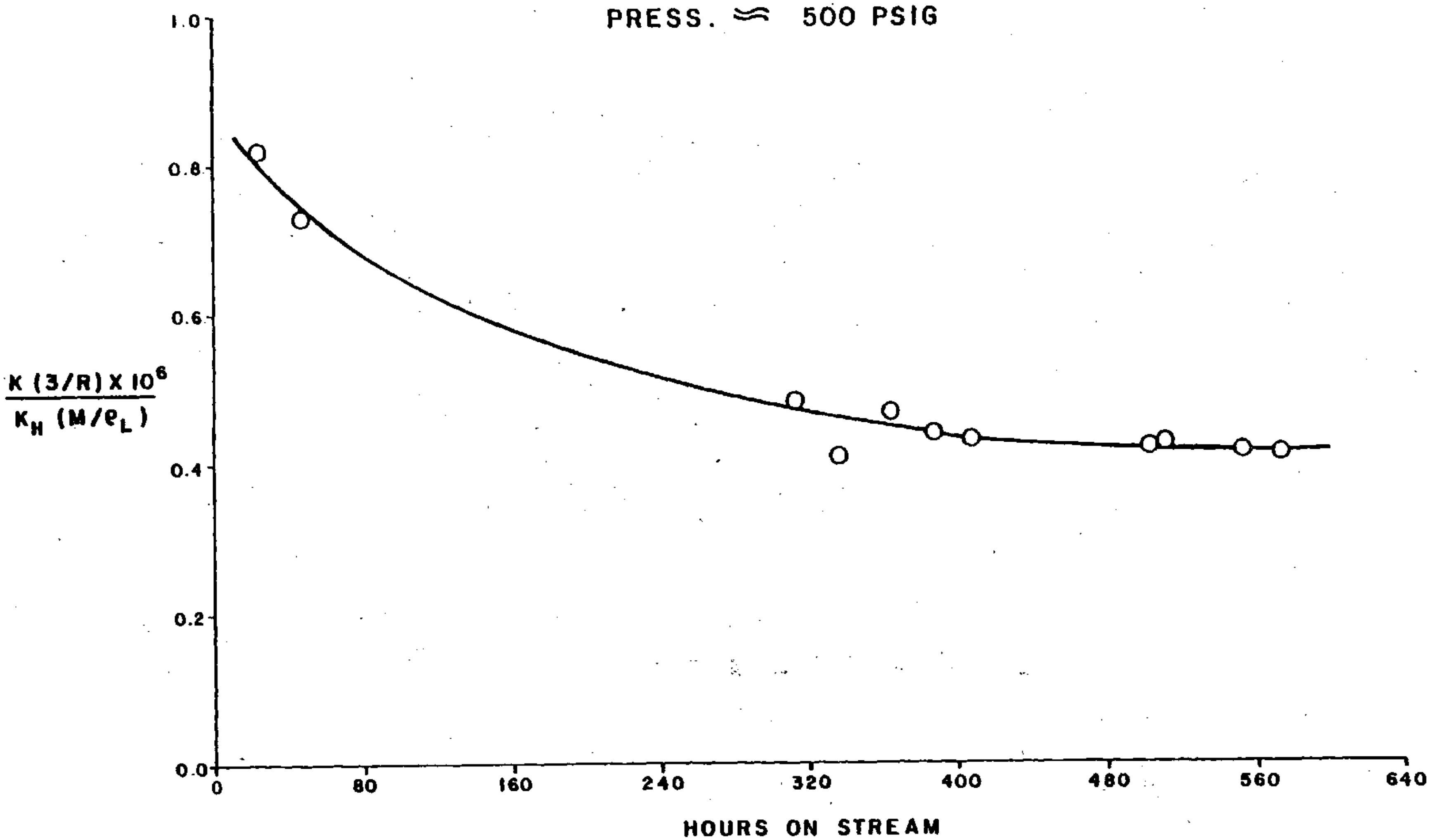
The life unit was put back on-stream using a $2H_2/CO$ feed gas with a CRG-A (12-16 mesh)/Witco 40 mineral oil system. The catalyst activity was monitored continuously for 290 hours and reached a value of 0.81 x 10^{-6} gm mole/gm cat-atm-sec. However, there were indications that a plug was developing in the reactor inlet and the operating condition was watched to follow this trend. After 310 hours, a plug developed which necessitated terminating the run. Examination of the reactor contents showed that the plug developed at the reactor inlet and was caused by excessive temperature, probably due to poor distribution of the circulating oil stream. The reactor was cleaned and new process tubing was installed. A fresh batch of Calsicat Ni-230S (1/16" spheres) catalyst was charged and reduced. The reactor was on-stream for about 600 hours using a $2H_2/1CO$ feed gas. The catalyst activity was monitored continuously and had equilibrated a k value of 0.41 x 10^{-6} gm moles/gm cat-atm-sec. Figure IV-B-1 shows the results to date for this run.

Another LPM/S life test (Calsicat Ni-230S/Witco 40 Mineral Oil and a 1.4 H_2/CO ratio) had been on-stream a total of 550 hours before a plug developed in the reactor oil inlet. Examination of the reactor contents showed that the plug developed at the reactor oil inlet and was caused by excessive temperatures, probably due to poor distribution of the circulating oil stream. The original design provided for the circulating oil entering the side of the reactor above the gas

FIGURE IV-B-1

LIFE TEST UNIT: ACTIVITY VS. TIME

CALSICAT Ni-230S
FEED GAS: 67% H_2 - 33% CO
TEMP. ≈ 350°C
PRESS. ≈ 500 PSIG



inlet. The reactor system was re-designed to alleviate this problem, by having the gas feed premixed with the circulating oil stream prior to entering the reactor.

Before termination of the run, the catalyst showed signs of equilibrating at $\sim 0.33 \times 10^{-6}$ gm mole/gm cat-atm-sec at $343^{o}C$ with a 1.4 H_2/CO feed gas as shown on Figure IV-B-2. The previous run with a $2H_2/Co$ feed gas showed that the catalyst equilibrated at a slightly higher value of 0.41×10^{-6} gm mole/gm cat-atm-sec. This difference is not significant in view of the difficulty in accurately reproducing the gas/liquid distribution patterns within the packed bed for the individual catalyst loadings.

Another test was started late 1975, with the same catalyst-oil system (Calsicat Ni-230S/Witco 40). The unit was on-stream for a total of 235 hours when a local power failure caused a contacting relay to freeze. This resulted in the salt bath temperature rising to well over $500^{o}C$. The high temperature caused damage to the unit. A backup temperature limit control system was installed to prevent a recurrence of this problem.

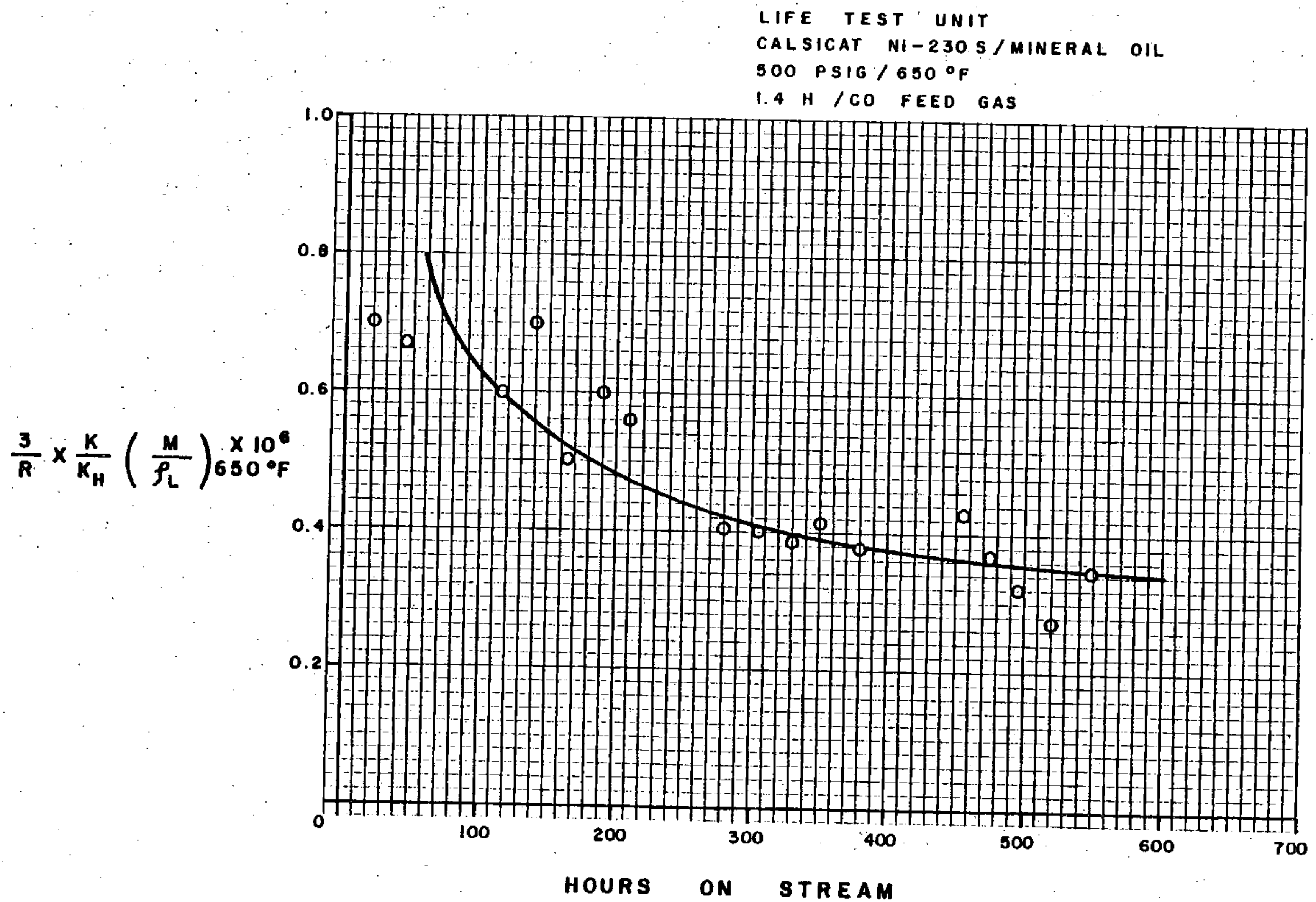
Before termination of the run, the catalyst activity had declined to a value of 0.38×10^{-6} gm mole/gm cat-atm-sec. Based on previous experience, this is a normal activity decline for this particular catalyst/oil sytem.

Several tests started during the fourth quarter 1975, had to be terminated due to local power failures, and resultant temperature run-aways. A high temperature limit control system was installed to prevent a recurrence of this problem.

In the first quarter 1976, the LPM/S life test unit was loaded with a Calsicat Ni-230S catalyst and run using a 1.4 H_2CO feed gas and a circulating stream of Witco 40 mineral oil. The operating conditions were as follows:

FIGURE IV-B-2

ACTIVITY vs. TIME



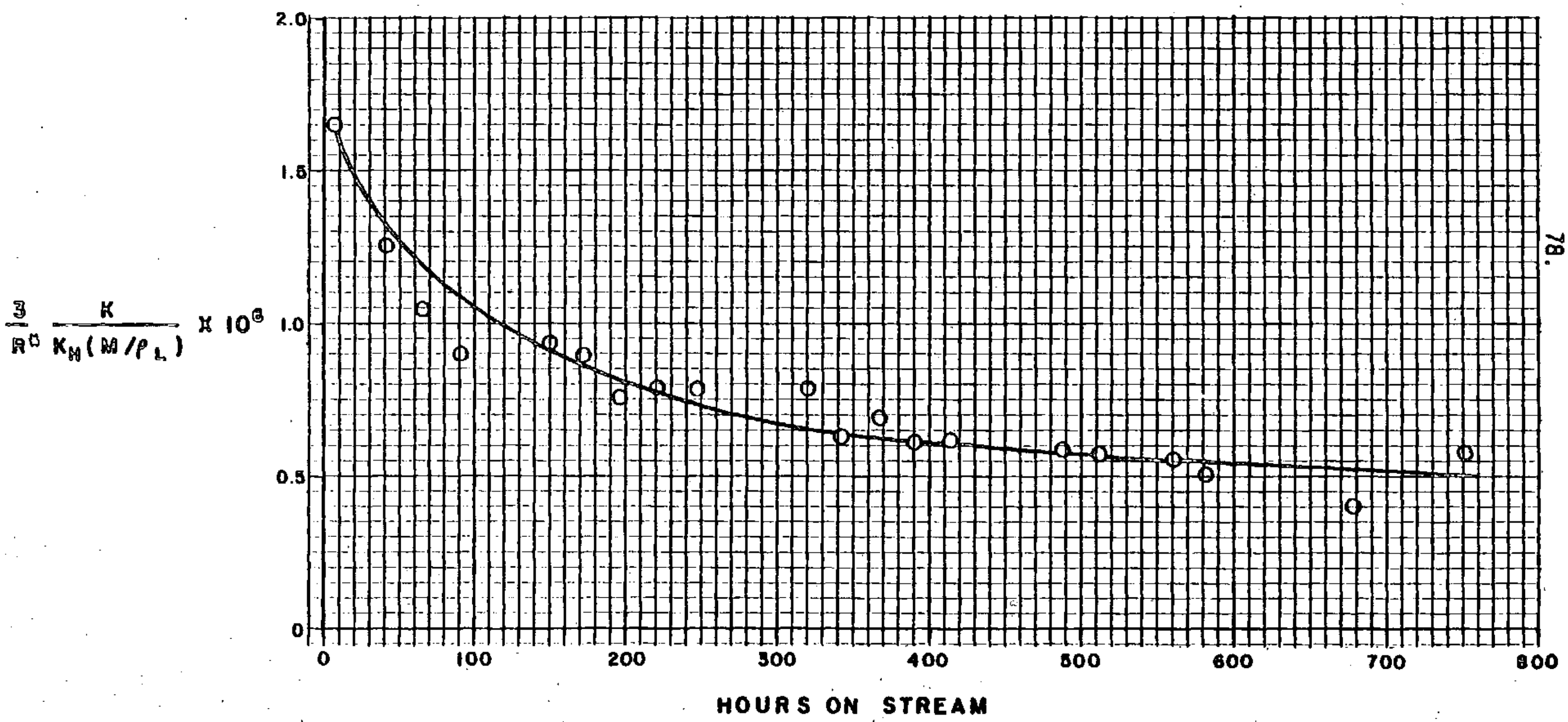
Pressure	500 psig
Salt Bath Temperature	313 ^{o}C
VHSV	2400 hr.$^{-1}$

Due to particulate matter in the feed gas line, a plug developed and the life test had to be terminated at 760 hours. This was somewhat sooner than the 1000 hour run that was planned. Figure IV-B-3 shows the catalyst activity during the test. The activity appeared to level off at a level equivalent to an activity constant corrected to 343^{o}C, of approximately 0.5 x 10^{-6} gm mole/gm cat.-atm.-sec. This activity was somewhat higher than the previous life test run for the same catalyst reported above. This completed work in the LPM/S life test unit.

FIGURE IV-B-3

ACTIVITY VS. TIME

LIFE TEST UNIT
CALISCAT NI-230S / WITCO 40 MINERAL OIL
500 PSIG / 650°F 1.4H_2/1CO FEED GAS



C. Polishing Reactor Unit

The two polishing reactor systems were completed and put on-stream at the end of July 1975, with a feed gas of the following nominal composition:

CO	2%
H_2	14%
CO_2	24%
CH_4	60%
	100%

This simulated a product gas from an LPM reactor using a $2H_2$/1CO feed gas. The reactor was loaded with 1/8" x 1/16" CRG-A catalyst.

The reactor salt bath was maintained at 300°C. With a feed gas VHSV of 10,000 hr^{-1}, the hot spot temperature was 400°C, located approximately 1 cm into the 6 cm bed. The location of the hot spot did not move, indicating little, if any, catalyst deactivation. After 265 hours on-stream, the product gas composition had remained constant at 78 percent CH_4 and 22 per CO_2 with no detectable quantities of either CO or H_2.

For the remainder of the 1000 hour run, the reactor salt bath was maintained at 300°C and the feed gas VHSV at 11300 hr^{-1}. The hot spot location, 1 cm into the 6 cm bed, remained constant during this time; however, the hot spot temperature, initially at 390-400°C, had fallen to 367°C. The product gas composition, however, remained constant over the range 77-79 percent CH_4 and 21-23 percent CO_2 with nil CO and H_2.

Late in 1975, a second one thousand (1000) hour test was completed with a polishing reactor containing CRG-A 1/8" 1 x 1/16" catalyst.

The feed gas to this unit had a composition that simulated the effluent gas from a LPM/S reactor when its feed gas composition is 1.4 H_2/1CO/0.36 H_2O. During the life of the run, the polishing reactor was operated at a VHSV of 9000 hr^{-1} and a salt bath temperature of 300°C. The hot spot location remained constant, 1 cm into the 6 cm bed, throughout the entire run. The initial hot spot temperature was 372°C. At 620 hours it was 348°C and at the end of the run it had fallen to 341°C. The effluent gas composition remained constant throughout the run at 60-61 percent CH_4, 39-40 percent CO_2, and less than 0.05 percent CO and H_2. At the end of the run, the catalyst was removed from the reactor and returned to the manufacturer for analysis.

Following the above run, the polishing reactors were modified for down-flow gas feed and to allow steam injection into Reactor B.

During the first quarter 1976, a one thousand (1000) hour test was completed on both Polishing Reactor A and Polishing Reactor B. Both reactors were loaded with CRG-A, 1/8" dia. x 1/16", catalyst. The conditions in Polishing Reactor A were set in order to simulate an effluent gas stream that would result from feeding a 1.4 H_2/1CO/0.36 H_2O synthesis gas to an LPM/S reactor operating at 900 psig and 650°F. The Polishing Reactor A feed gas had the following composition:

	Vol. %
H_2	6
CO	3
CO_2	36
CH_4	55
	100

A quantity of steam equal to 15 percent of the total dry gas feed was also fed to the polishing reactor. The operating conditions of Polishing Reactor A were:

Gas Flow	Down Flow
Pressure	500 psig
Salt Bath Temperature	$313^{o}C$
Feed Gas VHSV	10,100 $hr.^{-1}$

During the entire 1000 hour run, the hot spot temperature was $333^{o}C$ and remained in the same location, 3 cm into the 6 cm bed. The effluent dry gas composition remained constant at 38 percent CO_2, 62 percent CH_4 and traces of H_2 and CO.

The conditions of Polishing Reactor B were set in order to simulate an effluent gas stream from a LPM/S reator operating at 900 psig, $650^{o}F$ and with an initial feed gas of $2H_2/1CO$. The polishing Reactor B feed gas had the following composition:

	Vol. %
H_2	8
CO	2
CO_2	24
CH_4	66
	100

No steam injection was used in this run. The operating conditions of Polishing Reactor B were:

Gas Flow	Down Flow
Pressure	500 psig
Salt Bath Temperature	$313^{o}C$
Feed Gas VHSV	9600 $hr.^{-1}$

During the 1000 hour run, the hot spot temperature fluctuated between $337^{o}C$ and $343^{o}C$ and its location varied between 2 cm and 3 cm into the 6 cm bed. The effluent dry gas composition was measured at 26-28 percent CO_2 and 72-74 percent CH_4. Only traces of H_2 and CO were detected.

Upon completion of the 1000 hour run, both reactors were shut down. The catalyst was removed and returned to the vendor for detailed analysis.

In total, four 1000 hour tests were performed and after completion, catalyst analyses were performed by Grace Research Division on the CRG-A catalyst samples. The purpose of the polishing reactor studies was to simulate the performance of a commercial unit using dry product gases from LPM/S reactors operating with various synthesis gas feeds containing H_2/CO molar ratios less than 2/1. The nominal operating conditions for these four tests are shown in Table IV-C-1 and the results of the catalyst analyses are presented in Table IV-C-2.

TABLE IV-C-1

POLISHING REACTOR TEST CONDITIONS
CRG-A CATALYST, 1/8" Dia x 1/16"
Pressure - 500 psig

SALT BATH TEMPERATURE - 310°C

Test #	Gas Flow	Feed Gas Comparison; M% H_2	CO	CO_2	CH_4	Gas VHSV Hr.	Hot Spot Temperature 0 Hrs.	1000 Hrs.
1	Up	14.0	1.9	22.4	61.7	10,000	400°C	365°C
2	Up	6.3	3.0	35.5	55.2	9,000	370°C	340°C
3*	Down	6.2	2.9	35.0	55.9	10,100	335°C	335°C
4	Down	8.3	2.5	23.8	65.4	9,600	350°C	335°C

* Steam injection 0.10 - 0.15 moles per mole of dry gas feed.

In general, all four test runs operated smoothly throughout the 1000 hours. Aside from the changes in hot spot temperature (lowering) noted for three of the tests, all other observable parameters remained constant, e.g., hot spot location and product gas composition. Complete conversion of CO and H_2 was obtained in all runs. However, after analyses

Table IV-C-2

Polishing Reactor Test Catalyst Analyses: CRG-A (1/8" ø x 1/16")

Test No.	Catalyst Sample Position	% Carbon in Sample	Nickel S.A., M^2/gram	-Alumina or Nickel Aluminate	BET S.A., M^2/gram	Average Pore Diameter, A°
Unused Catalyst	-	3.1-3.4 (oxide) 3.7-4.0 (reduced)	-	-	175 (oxide) 110-130 (reduced)	80-90 (oxide)
1	In	8.5-20	Low	Yes	100	165
	Middle	4.8	Normal	No	100	165
	Out	4.2	Normal	No	100	160
2	In	27.6	Normal	Yes	190*	125
	Middle	15.4	Normal	No	140	120
	Out	6.9	Normal	No	130	110
3	In	4.4	NA	No	60**	240**
	Middle	3.0	NA	No	70**	210**
	Out	3.1	NA	No	70**	210**
4	In	18.0	NA	No	130	135
	Middle	5.5	NA	No	110	135
	Out	3.7	NA	No	110	135

*High value due to excessive carbon laydown.

**Normal values associated with effect of steam addition.

of the spent catalyst from Tests 1 and 2 were received, the high carbon laydown and the presence of α-alumina and nickel aluminate prompted several changes to the equipment before initiating Tests 3 and 4.

The presence of α -alumina and nickel aluminate at the reactor inlet indicated that catalyst site temperatures in excess of 650^{o}C had occured, despite the significantly lower observed bulk temperature. Since the reactors had operated in an upflow manner, it was possible that highly reactive fine catalyst particles (dusting from the catalyst tablets) might have settled in the bottom thereby creating high catalyst site temperatures. This might also explain the excessively high carbon content of the inlet catalyst samples since the high temperatures would thermodynamically favor the formation of carbon.

For these reasons, Tests 3 and 4 were run with a downflow feed pattern. In addition, Test 3 investigated the effect of a low level of steam injection on catalyst performance. As the results in Table IV-C-2 indicate, no α-alumina or nickel aluminate were formed in either Test 3 still fairly high ($\sim$ 18 weight percent), there was virtually no effect on the important catalyst parameters. More importantly, Test 3, with low level steam injection, showed virtually zero carbon laydown as well as a constant hot spot temperature throughout the 1000 hour test. While the BET surface area and average pore diameters are significantly different from the results in the other three tests, the manufacturer has reported that these values are a typical result of steam addition.

Based on this work, it is fairly certain that the long term operation of polishing reactors running on LPM/S product gases is commercially practical, providing low level steam injection is used. The optimum level of steam addition will be very small, most likely on the order of 0.03-0.05 moles steam/mole gas. There will probably be sufficient water left in the gas, following cooling and condensation, to avoid any additional injection of steam.

D. Process Development Unit

1. Calsicat Ni-230S/Witco 40 Mineral Oil Reaction Rate Studies w/$2H_2$/1CO feed gas

The overhaul and modifications of the PDU to allow combined liquid phase methanation/shift operation were completed on schedule. A small problem was encountered during checkout of the seal flush system. Dismantling the process liquid pumps revealed that the holes for the seal flush oil were only partially bored through, resulting in high pressure drops across the seals. A local machine shop was able to correctly rebore the holes. Other modifications included installation of the water injection pump, recalibration of the X-ray detector and calibration of the flow controls. The PDU was pressure tested and a process variable scan was started in February, 1976. The system investigated was the Calsicat Ni-230S/Witco 40 mineral oil system using a $2H_2$/1CO feed gas. The main objective of this test program was to demonstrate the feasibility of the LPM/S reaction on a larger scale and compare the reactor performance for the results obtained in both the bench scale and process development units.

Table IV-D-1a summarizes all the data obtained during the complete process variable scan. The catalyst activity is based on the reaction rate model (Equation 1) as derived for the combined shift/methanation system.

Figure IV-D-1a shows the catalyst activity as a function of time for all the PDU runs. Base case conditions were repeated periodically during the entire run and the catalyst activities are shown as black dots for these runs. The catalyst reached constant activity after approximately 50 hours on stream. Figure IV-D-1b shows the catalyst activity correction factor used to evaluate the results. Figure IV-d-1c shows the data plotted according to the kinetic expression

Table IV-D-1a

PDU Process Variable Scan
Calsicat Ni-230S*/Witco 40 Mineral Oil
Feed Gas: 67% H_2, 33% CO

Run No.	Temp. °F	Pressure psig	VHSV Hr^{-1}	CO Conv. %	$\frac{k \times 10^6}{K_H(M/\rho_L)_T}$	$\frac{k \times 10^6}{K_H(M/\rho_L)_{650^oF}}$	$\frac{3}{R} \times \frac{k}{K_H(M/\rho_L)_{650^oF}}$	Effluent H_2/CO Ratio
1-1	597	500	3250	94.4	1.60	2.45	3.78	1.91
1-2	651	500	3320	98.7	2.56	2.50	3.87	6.83
1-3	599	500	3370	88.6	1.25	1.88	2.90	1.26
1-4	598	500	4335	83.2	1.20	1.81	2.79	1.20
1-5	603	500	2100	97.2	1.29	1.87	2.88	3.50
1-6	602	500	3140	88.9	1.18	1.73	2.67	1.36
1-7	551	500	2095	89.5	0.80	1.81	2.80	1.36
1-8	601	500	3110	83.5	0.96	1.41	2.18	1.40
1-9	552	500	1405	95.8	0.76	1.71	2.64	3.09
1-10	553	500	2155	77.7	0.55	1.23	1.90	1.25
1-11	650	500	3440	93.3	1.59	1.59	2.45	1.81
1-12	600	500	3440	76.0	0.84	1.25	1.93	1.05
1-13	650	500	3470	89.1	1.34	1.34	2.07	1.64
1-14	599	500	3460	69.8	0.71	1.06	1.65	1.01
1-15	649	500	880	99.6	0.85	0.86	1.32	10.00
1-16	652	500	2450	95.1	1.16	1.16	1.79	2.62
1-17	652	500	4200	77.6	1.09	1.09	1.69	1.26
1-18	650	500	3165	86.1	1.03	1.03	1.59	1.48
1-19	650	900	4345	94.7	1.26	1.26	1.82	2.38
1-20	651	900	3425	98.3	1.30	1.29	1.87	5.18
1-21	650	900	6205	86.8	1.06	1.06	1.53	1.38
1-22	650	900	3775	97.6	1.23	1.23	1.79	4.09
1-23	645	900	5015	91.1	0.97	0.98	1.41	1.74
1-24	651	900	4320	92.5	1.03	1.02	1.47	1.88
1-25	649	900	4177	95.5	1.24	1.25	1.81	2.66
1-26	600	900	2315	90.3	0.75	1.11	1.89	2.22
1-27	604	900	2975	97.1	1.11	1.15	1.66	3.25

*Catalyst loading = 5475 grams

FIGURE IV-D-1a

CATALYST ACTIVITY VS. TIME

PROCESS DEVELOPMENT UNIT

CALISCAT NI-230S / WITCO 40 MINERAL OIL

500-900 PSIG / 650°F $2H_2/1CO$ FEED GAS

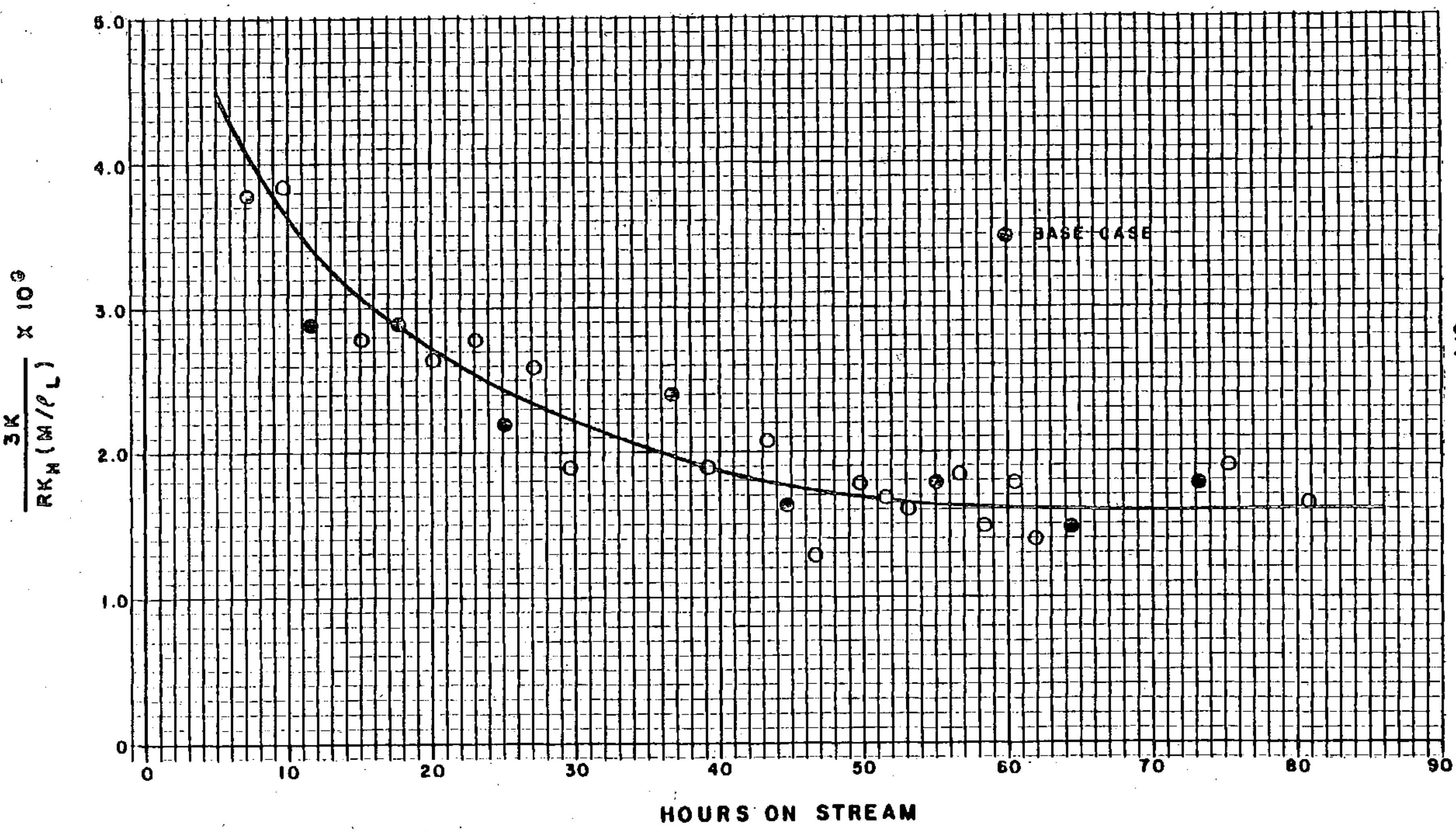


FIGURE IV-D-1b

ACTIVITY CORRECTION FACTOR VS. HOURS ON STREAM

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