C. Laboratory Support Work

1. Evaluation of CRG-A Catalysts

As part of the LPM Pilot Plant development, Chem Systems had an ongoing program of evaluating commercial catalyst forms for use in the pilot plant and eventual commercial size plants. In conjunction with this program, several formulations were prepared by LDI Catalyst Company, a division of W. R. Grace.

A tableted form of CRG-A catalyst was tested in the bench scale unit with Witco-40 mineral oil at 340°C and 900 psig. A poor reactivity 0.2-0.3 x 10^{-6} gm-mol/(atm-gm catalyst-sec), was observed during the first day of operation. When starting up on the second day, a plug developed and the reactor was shut down. The reactor was opened and portions of the catalyst were found in good shape. However, part of the catalyst was wedged into the upper portion of the reactor by the 600 psi pressure drop encountered during the startup.

A second run was made with a fresh batch of tableted catalyst under the same reactor conditions as the previous run. This time, a rate constant of 3-5x10^{-6} gm-mol/atm-gm catalyst-sec was obtained on the first day. Again, a plug developed during startup on the second day. The catalyst was, again, found to be in good shape except for the portion wedged in the top of the reactor.

The reactor was modified for future use by removing the thermocouple internals to prevent plugging from occurring.

A third run was made in the bench scale unit with CRG-A tablets (3/32" dia. X 3/32") and Witco 40 mineral oil at 500 psig and 316-340°C. The feed gas contained 75 percent H_2 and 25 percent CO. A reactivity of 4-6 X 10^{-6} gm mol/(atm-gm catalyst-sec) was observed during the one-day

run. The unit was shut down and the catalyst removed for visual inspection. The material looked good, i.e., there was no evidence of attrition or breakage.

A 90-hour round-the-clock continuous run was performed during September 1976, with CRG-A (3/32" dia. X 3/32") tablets and Witco 40 mineral oil at 500 psig and 330-345°C using a 3 H_2/CO feed gas. Initially, the reactivity was 5-6 X 10^{-6} gm mol/(atm-gm catalyst-sec) and it slowly decreased to 4.5 X 10^{-6} over the first 18 hours (see Figure IV-C-1). There was an unexplained rapid loss in activity over the next four hours and then, the activity equilibrated at a value of 1 X 10^{-6} for the next 65 hours. The catalyst was returned to LDI Catalyst Company for analysis to determine the cause of the activity loss.

An eighty-hour round-the-clock continuous run was performed in the bench scale unit with CRG-A extrudates (3/32" dia.) and Witco 40 mineral oil. A 3 H_2/CO feed gas was used and the reactor conditions were 500 psig and 340-345°C. Initially the reactivity was 9-10 X 10^{-6} gm-mol/(atm-gm catalyst-sec) and it equilibrated at 5 X 10^{-6} after approximately 50 hours. Figure IV-C-2 shows the catalyst activity as a function of operating time. The run was voluntarily terminated at 80 hours. The physical appearance of the material when removed from the reactor was good. Samples of this used catalyst were also returned to LDI Catalyst Company for analysis.

The excellent behavior of this catalyst during the continuous run can be taken as evidence that a poisoning-type failure was responsible for the sudden activity loss experienced after 18 hours on-stream with the previous batch of catalyst.

A run was made in November, 1976, in the Process Development Unit testing the commercial preparation of CRG-A tablets (3/32" dia. X 3/32") with a $2H_2/CO$ feed gas and Witco 40 mineral oil. The run was conducted in

FIGURE IV-C-1

CONTINUOUS RUN

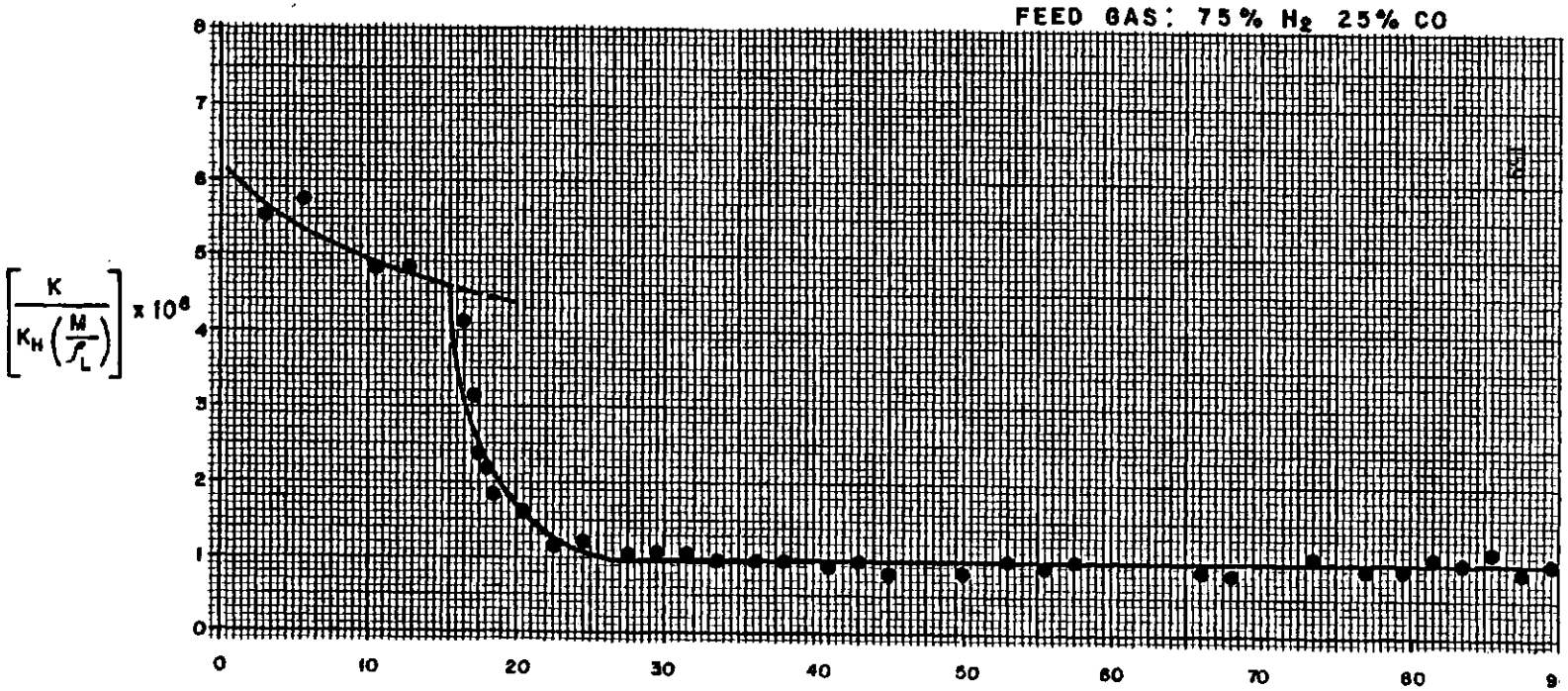
CRG-A $^{3}/_{32}$" ϕ x $^{3}/_{32}$" TABLETS

WITCO 40 OIL

500 PSIG

650 °F NOMINAL TEMPERATURE

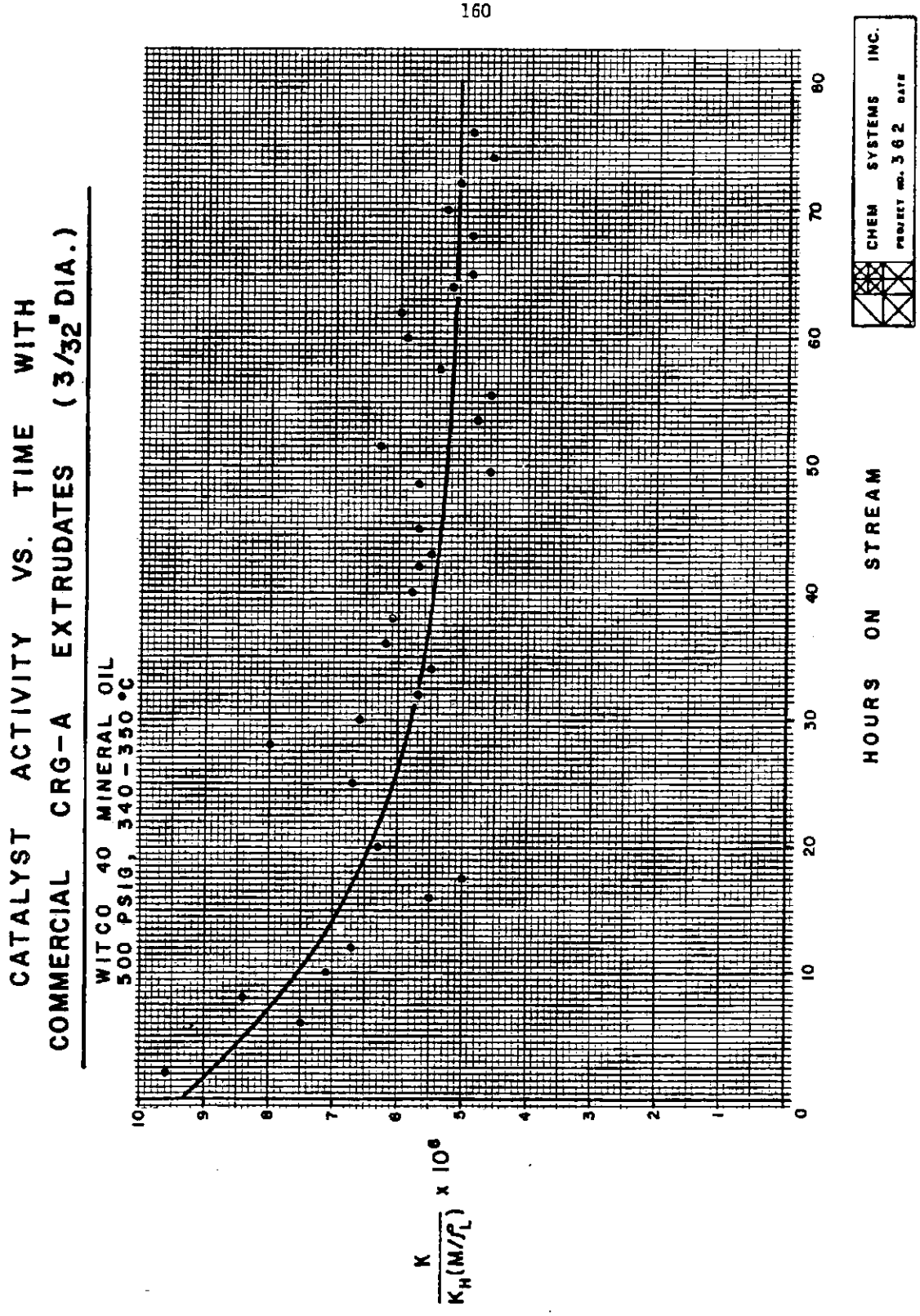
FEED GAS: 75% H_2 25% CO



CHEM SYSTEMS INC.

PROJECT NO. 664 DATE

FIGURE IV-C-2


CATALYST ACTIVITY VS. TIME WITH
COMMERCIAL CRG-A EXTRUDATES (3/32" DIA.)
WITCO 40 MINERAL OIL
500 PSIG, 340-350 °C
$\frac{K}{K_H(M/\rho_L)} \times 10^6$
HOURS ON STREAM
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
10
CHEM SYSTEMS INC.

double-shift operation. Table IV-C-1 summarizes the results. The catalyst activity stabilized after a few hours with a rate constant of 1.5-1.75 X 10^{-6} and remained at that activity for the duration of the 92-hour run. This is comparable to prior experience with this catalyst.

Figure IV-C-3 shows the catalyst activity during the course of the run. Figure IV-C-4 is an Arrhenius plot showing the effect of reaction temperature on catalyst activity. From these data, an activation energy of 10,200 cal/gm mol was calculated. This is also typical for this catalyst in PDU operation.

A second PDU run was performed with CRG-A extrudates (3/32" dia X 3/32"), commercial preparation, using a $2H_2/CO$ feed gas and Witco-40 mineral oil. The results of this run, which lasted 68 hours, are presented in Table IV-C-2. Figure IV-C-5 shows catalyst activity as measured by a kinetic rate constant for the duration of the run. The catalyst activity leveled out after 45 hours at a rate constant of 3.0 X 10^{-6}. Although this is somewhat less than the 5 X 10^{-6} obtained in a bench scale run during September, the result is still very encouraging. Figure IV-C-6 shows the activity correction factor used to put all the data on a common basis for evaluation. Figure IV-C-7 is an Arrhenius plot showing the effect of temperature for the CRG-A extrudates. An activation energy of 13,800 cal/gm mol was calculated for this catalyst.

During the middle of this run, Witco-40 mineral oil was replaced with Freezene-100, a Witco product with a lower pour point (-35°F). No adverse effects were noticed with this oil. Therefore, this oil was used in the LPM Pilot Plant at IGT's HYGAS Plant in Chicago where cold weather could cause freeze-up of the Witco 40.

2. Evaluation of an Engelhard Catalyst

A third run in the PDU tested an Engelhard supported nickel catalyst. Freezene-100 mineral oil was used as the process liquid, along with a

TABLE IV-C-1

PDU PROCESS VARIABLE SCAN
CRG-A TABLETS/WITCO 40 MINERAL OIL

Feed Gas: 68% H_2, 32% CO
Pressure: 500 psig
Catalyst Weight: 5000 grams
Catalyst Volume: 0.12 $Ft.^3$ (3/32" dia. x 3/32" tablets)

Run No.	Temp ^oF	VHSV Hr^{-1}	CO Conv %	$\frac{K \times 10^6}{K_H(M/\rho_2)_T}$	$\frac{K \times 10^6}{K_H(M/\rho_2)_{650^oF}}$	$\frac{3K \times 10^6}{RK_4(M/\rho_2)_{650^oF}}$
1-1	629	8040	68.7	1.09	1.27	2.01
-2	629	8840	68.7	1.02	1.21	1.91
-3	630	8465	64.6	1.03	1.22	1.93
-4	637	7905	63.0	0.92	1.01	1.60
-5	636	7880	61.9	0.96	0.99	1.57
-6	630	7550	63.1	0.88	1.02	1.61
-7	651	7735	76.1	1.29	1.28	2.04
-8	576	3640	75.4	0.59	1.04	1.65
-9	629	4225	87.1	0.94	1.04	1.87
-10	651	4745	82.6	0.97	0.96	1.60
-11	599	4030	73.6	0.63	0.95	1.51
-12	651	2850	93.6	1.05	1.04	1.68
-13	625	2825	95.8	.91	1.00	1.59
-14	570	2765	81.1	0.53	0.96	1.52
-15	601	2940	90.7	0.81	1.18	1.63
-16	651	2930	96.6	1.17	1.18	1.62
-17	653	8120	72.1	1.23	1.21	1.66
-18	655	5860	81.5	1.17	1.13	1.56
-19	675	5815	85.1	1.32	1.10	1.52
-20	650	3025	95.1	1.08	1.08	1.50
-21	590	3010	84.5	0.65	1.04	1.43
-22	621	3025	91.1	0.85	1.07	1.48
-23	622	5765	70.0	0.81	1.01	1.39
-24	672	3170	97.1	1.24	1.08	1.49
-25	620	3015	92.5	0.91	1.10	1.52
-26	618	7535	64.6	0.91	1.13	1.55
-27	670	7860	79.9	1.53	1.28	1.76
-28	671	3125	97.7	1.39	1.16	1.60
-29	672	5775	83.7	1.24	1.19	1.64
-30	620	7475	69.8	1.04	1.27	1.75
-31	668	3845	95.3	1.37	1.16	1.60
-32	651	3915	92.1	1.16	1.12	1.54
-33	570	3900	78.0	0.69	1.23	1.64
-34	602	3900	85.4	0.88	1.27	1.69
-35	570	3800	79.6	0.72	1.36	1.89
-36	620	3025	97.68	1.23	1.54	2.12
-37	677	3005	100.0	-	-	-
-38	601	3045	93.2	0.97	1.41	1.94
-39	651	3020	99.4	1.73	1.72	2.37
-40	599	2800	94.0	0.91	1.35	1.85
-41	604	4880	77.1	0.83	1.18	1.61
-42	571	4735	69.2	0.65	1.21	1.65
-43	675	3680	96.3	1.43	1.20	1.64
-44	622	3610	87.0	0.87	1.07	1.46

FIGURE IV-C-3

CATALYST ACTIVITY VS. TIME

PROCESS DEVELOPMENT UNIT

CRG-A TABLETS/WITCO 40 MINERAL OIL

500 PSIG $2H_2/ICO$ FEED GAS

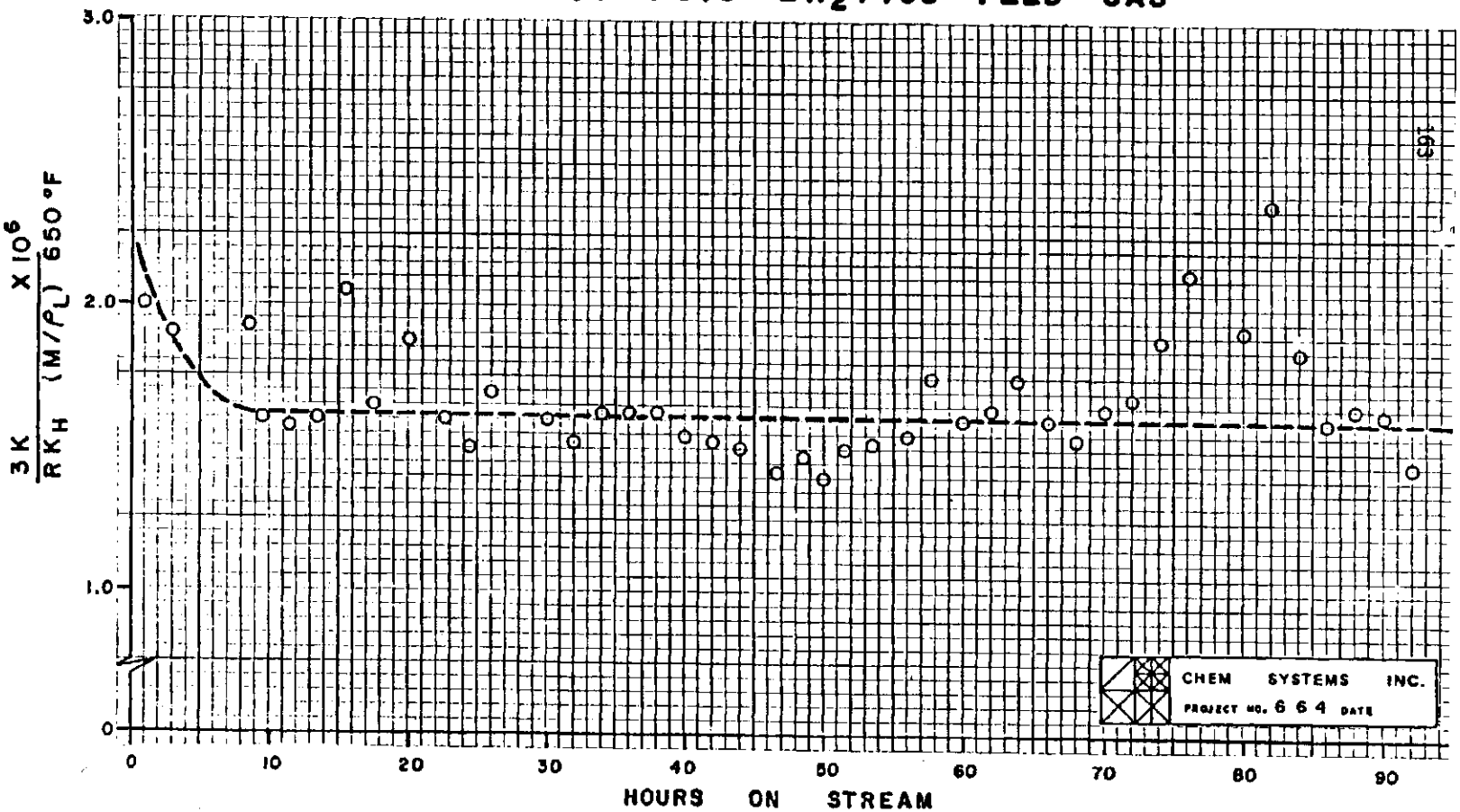


FIGURE IV-C-4

KINETIC RATE CONSTANT VS. TEMPERATURE

PROCESS DEVELOPMENT UNIT
CRG-A TABLETS / WITCO 40
500 PSIG $2H_2$ / CO FEED GAS

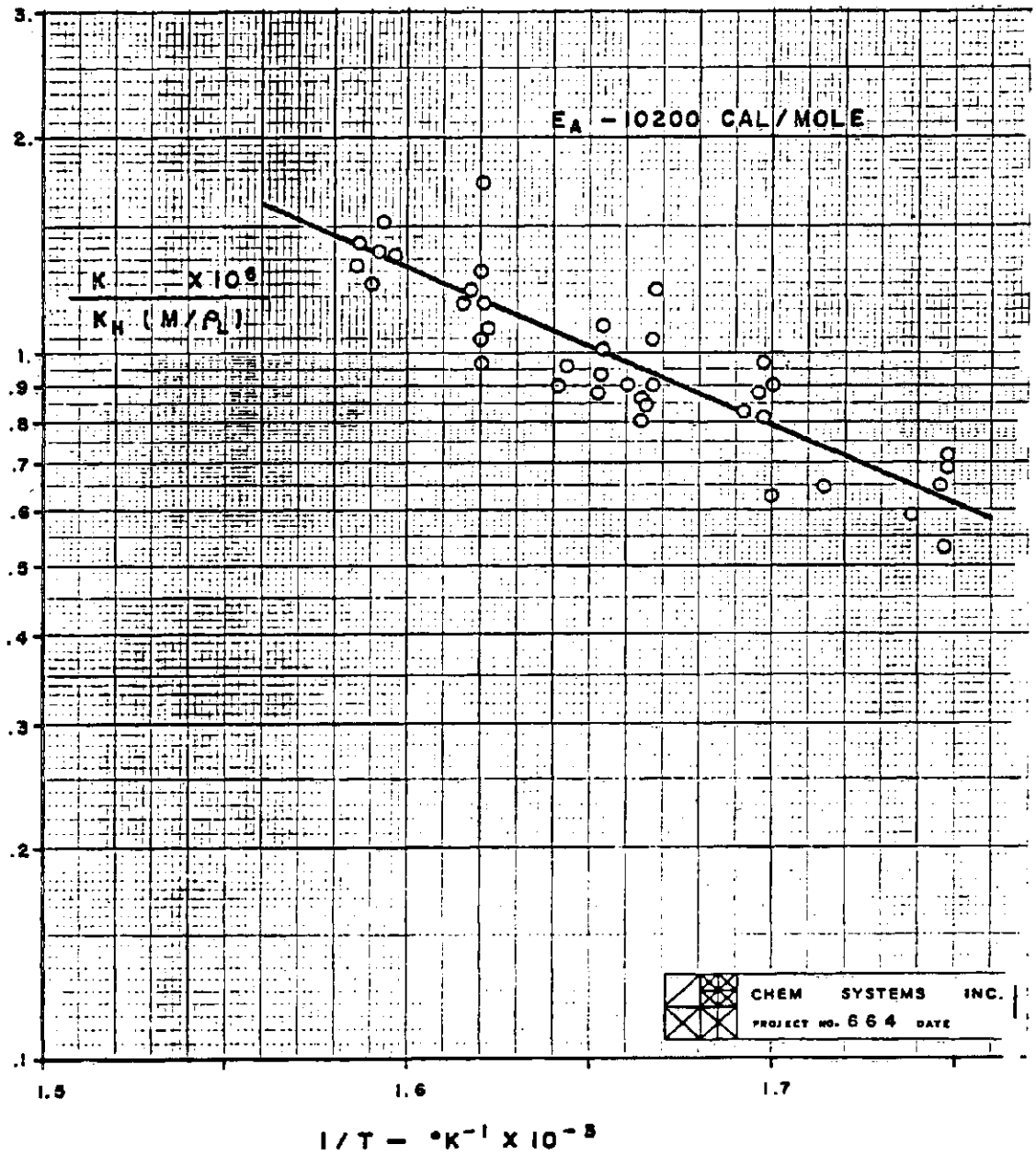


TABLE IV-C-2

PDU PROCESS VARIABLE SCAN
CRG-A EXTRUDATES/WITCO 40 MINERAL OIL

Feed Gas: 68% H_2, 32% CO
Pressure: 500 psig
Catalyst Weight: 5,000 grams
Catalyst Volume: 0.12 $Ft.^3$

Run No.	Temp ^oF	VHSV HR^{-1}	CO Conv %	$\frac{K \times 10^6}{K_H(M/\rho_L)_T}$	$\frac{K \times 16^6}{K_H(M/\rho_L)_{650^oF}}$	$\frac{3K \times 10^6}{RK_H(M/\rho_L)_{650^oF}}$
2-1	645	7955	98.2	3.75	3.86	5.94
2-2	611	6715	92.2	2.01	2.74	4.21
2-3	600	6060	91.2	1.72	2.53	3.89
2-4	597	2690	99.9	2.69	4.04	6.22
2-5	597	5290	94.8	1.64	2.47	3.80
2-6	621	6850	94.6	2.24	2.79	4.29
2-7	642	6645	96.0	2.52	2.67	4.11
2-8	642	6850	93.8	2.25	2.38	3.67
2-9	604	3405	98.1	1.59	2.26	3.47
2-10	622	5265	91.3	1.51	1.87	2.87
2-11	640	7670	87.9	1.91	2.06	3.14
2-12	640	4955	96.3	1.93	2.07	3.16
2-13	601	3605	94.3	1.21	1.76	2.68
2-14	586	5800	74.1	0.92	1.50	2.29
2-15	640	4845	96.7	1.95	2.10	3.08
2-16	662	4885	97.5	2.14	1.96	2.88
2-17	596	4795	85.4	1.08	1.64	2.40
2-18	632	4935	96.2	1.91	2.18	3.27
2-19	656	4870	98.9	2.65	2.53	3.80
2-20	592	5010	88.9	1.29	2.02	3.03
2-21	590	2230	99.6	1.44	2.29	3.44
2-22	636	4830	95.6	1.77	1.96	2.98
2-23	603	3855	93.8	1.26	1.80	2.74

FIGURE IV-C-5

CATALYST ACTIVITY VS. TIME
PROCESS DEVELOPMENT UNIT
CRG-A EXTRUDATES/WITCO 40 MINERAL OIL
500 PSIG $2H_2$/1CO FEED GAS

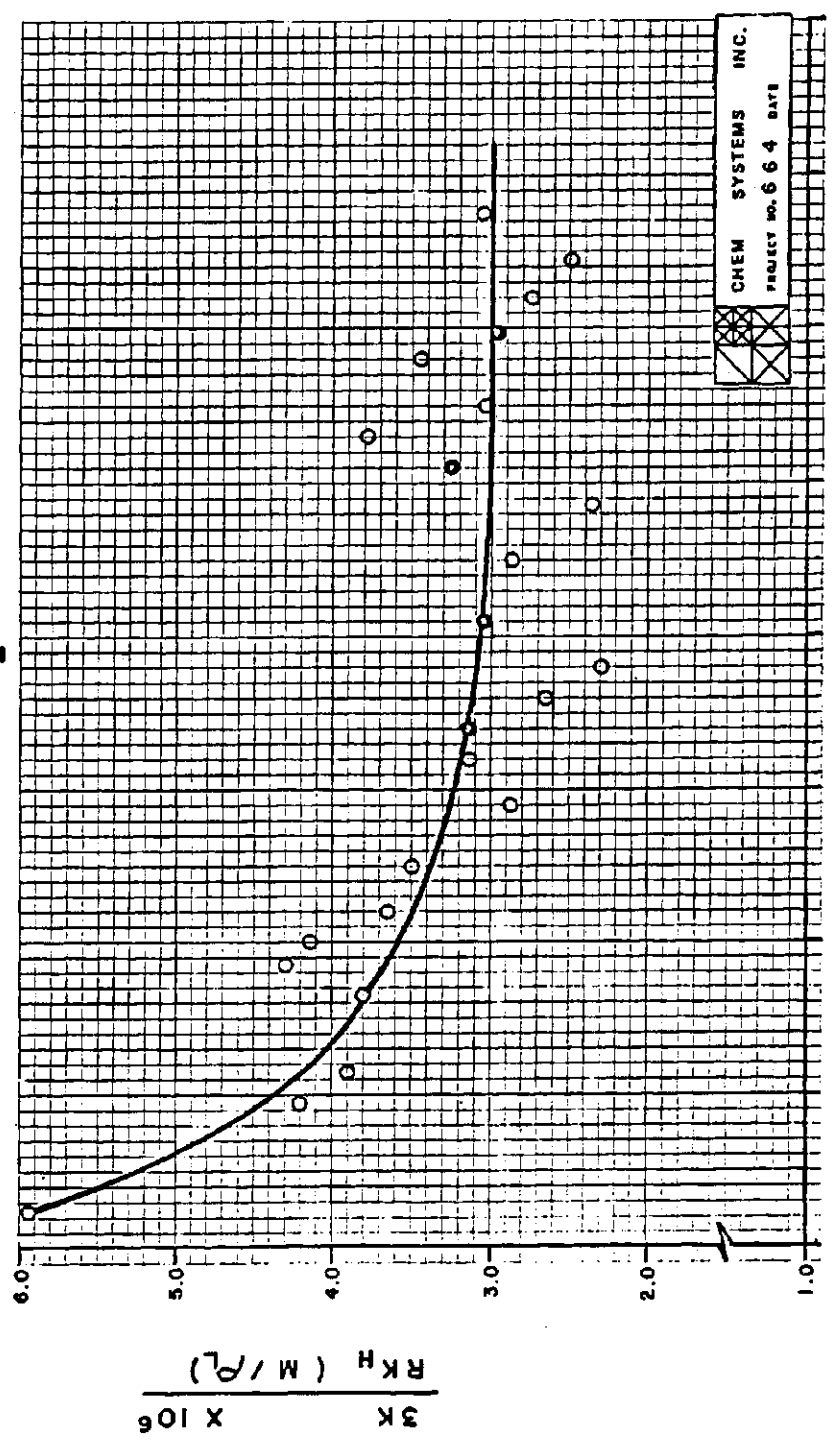


FIGURE IV-C-6

ACTIVITY CORRECTION FACTOR VS. HOURS ON STREAM
PROCESS DEVELOPMENT UNIT
CRG-A EXTRUDATES/WITCO 40 MINERAL OIL
500 PSIG $2H_2/CO$ FEED GAS

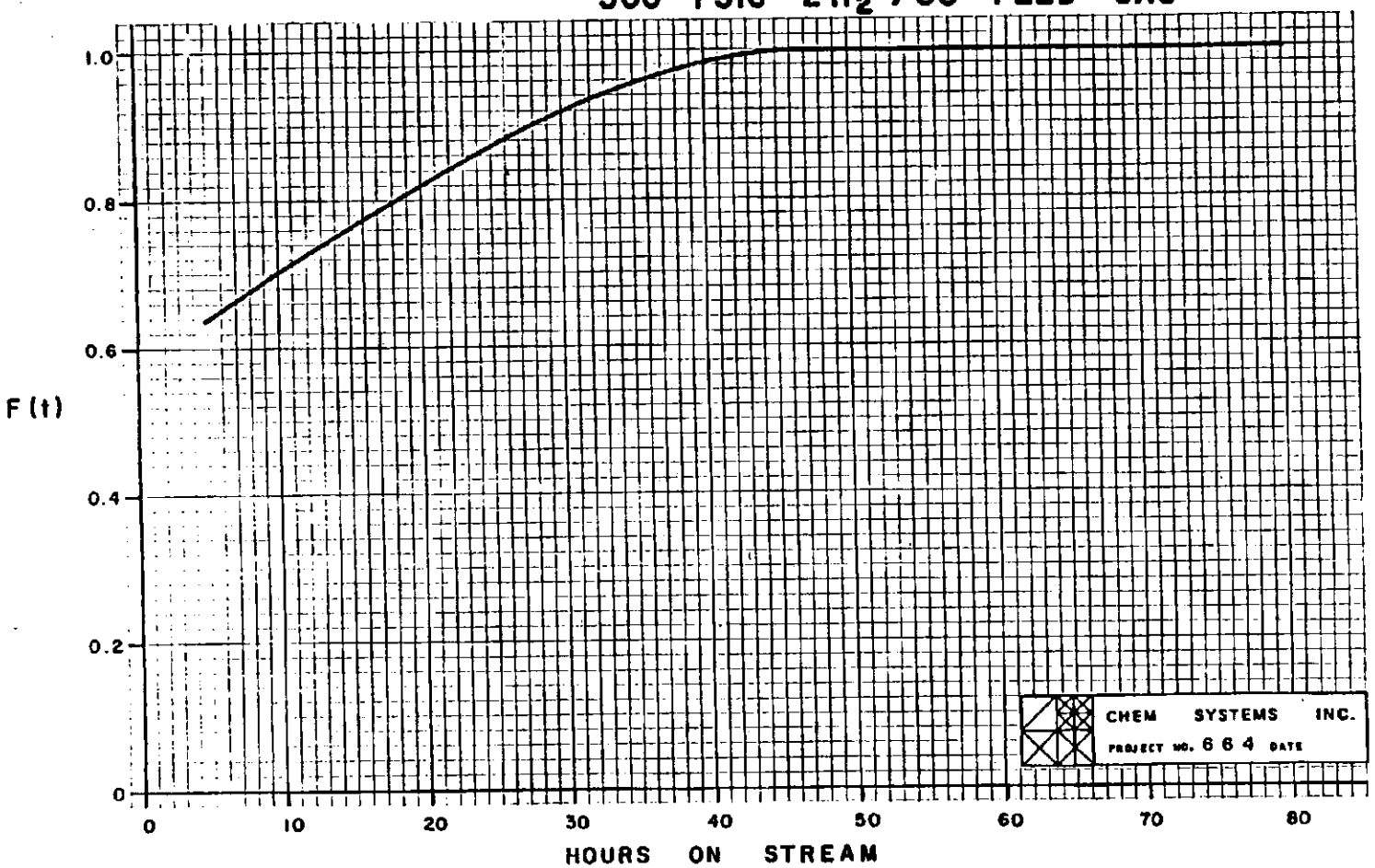
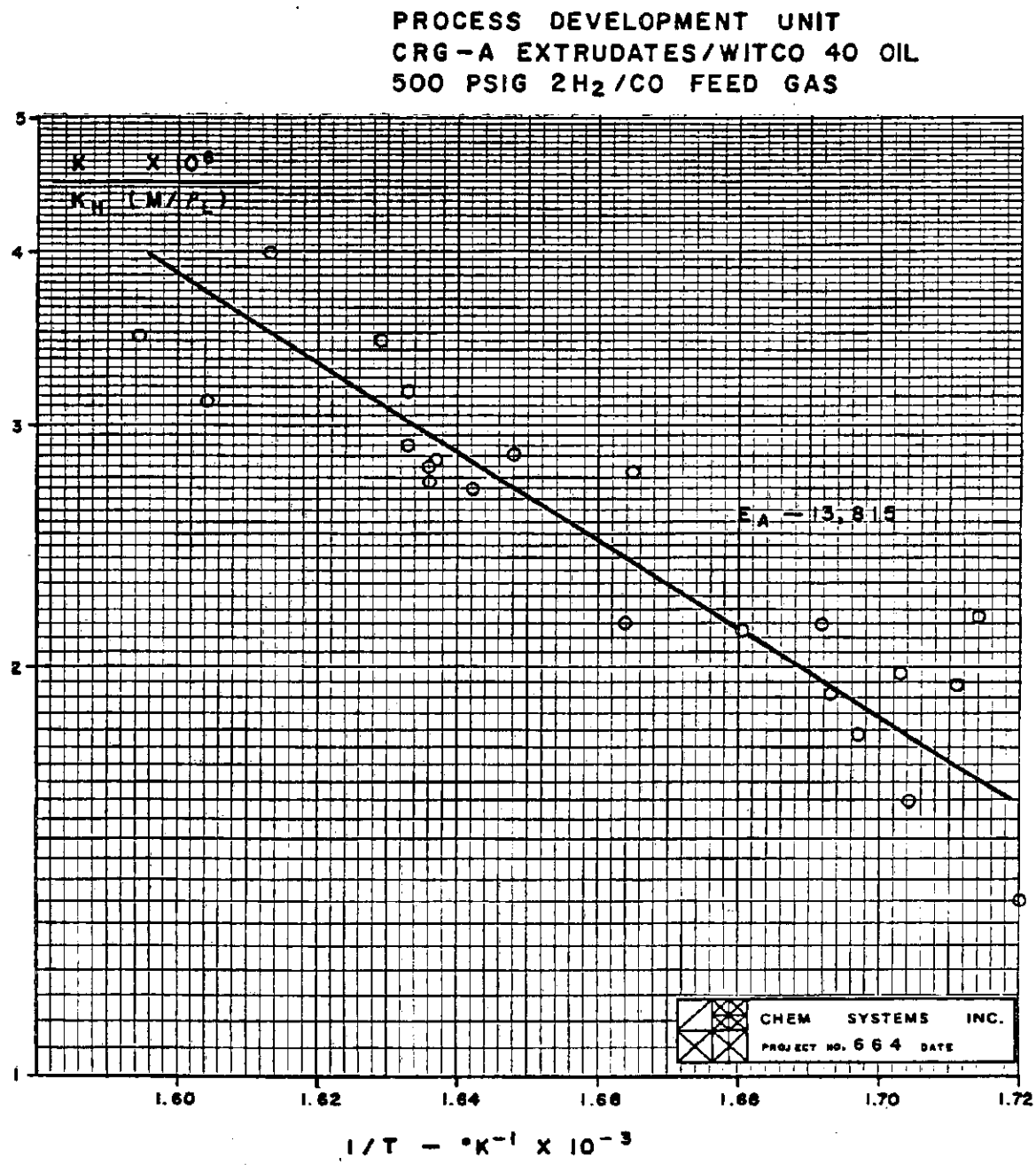


FIGURE IV-C-7

KINETIC RATE CONSTANT VS. TEMPERATURE



$2H_2/CO$ feed gas. The initial activity level was calculated to be 1.5 X 10^{-6} gm mol/(sec-atm-gm catalyst). Over a period of three to four days, the activity equilibrated at a value of about 0.9 - 1.0 X 10^{-6} gm mol/(sec-atm-gm catalyst). This value is consistent with earlier bench scale unit data.

3. Pilot Plant Support Studies with Calsicat Catalyst

The bench scale unit was run to test the use of a $6H_2/CO$ feed gas similar to that produced by the HYGAS reformer and check the validity of the reaction model under conditions expected in the LPM Pilot Plant with this gas. The results are presented in Table IV-C-3. Feed gas was alternated between the standard $3H_2/CO$ and the simulated reformer gas ($5H_2/CO$). Each time the feed gas was switched to $6H_2/CO$, the catalyst activity doubled, which is the expected result according to the LPM reaction model. This provided the necessary information to modify the test program for the LPM Pilot Plant.

Freezene-100 oil samples from various points in the pilot plant were sent to Chem Systems' Fairfield Laboratories in January, 1977 to check earlier IGT analyses. An independent firm reported sulfur content of under 2 ppm. Checking into the analytical procedures used earlier at IGT revealed that the techniques used were inadequate for such low concentrations.

The pilot plant methanation data taken from Runs #1 and #2 were reviewed. It was decided to conduct some tests on samples of catalyst from the pilot plant in an effort to determine the reason for the observed low reaction rate constants. An inadequate catalyst reduction procedure was suspected. Catalyst samples were delivered to Chem Systems' Research Center, feed gases were ordered and preparations were begun for testing these samples in the LPM bench scale unit. The original plans called for two (2) tests of the Calsicat catalyst in the BSU.

TABLE IV-C-3

BENCH SCALE UNIT
TEST OF 6 H_2/CO FEED GAS

Oil: Witco-40
Catalyst: Calsicat No. 230-S (1/16" Sperodized Extrudates)
Pressure: 550 psig
Catalyst Weight: 118 gm
Catalyst Volume: 192 cc

Date	Time	T(F°)	Gas (L/H)	Conv. (%)	$K_{650°F}$ (X 10^6)	Feed Gas Comp.	
						H_2(%)	CO(%)
10/25	1500	620	1217	95.9	5.1	75	25
10/26	1200	630	1316	93.7	4.0	75	25
	1530	632	1410	97.3	5.5	75	25
	1600	617	1269	91.6	4.0	75	25
10/27	1300	594	1227	81.1	3.5	75	25
	1430	592	1168	87.9	5.9	84	16
	1600	594	824	96.0	6.2	84	16
10/28	1215	596	1591	76.1	5.0	84	16
	1445	637	1643	88.3	4.8	84	16
	1600	644	1321	88.8	2.7	75	25
10/29	1400	600	1164	67.9	2.1	75	25
	1445	592	1224	82.3	5.0	84	16
	1700	633	1210	94.6	4.9	84	16

In the first test, the catalyst would be reduced as if it were in the inactive oxide form. In the second text, the catalyst would be reduced in the same manner as was the pilot plant charge.

In mid-July, 1977, a 200-gram sample of Calsicat Ni-230 S used in the pilot plant was loaded in the BSU and rigorously reduced. The catalyst was heated up under a N_2 purge at a rate of 100°C/hr to 180°C. The purge gas was changed to H_2, and heating was continued at a new rate of 50°C/hr to 425°C. The bed was then maintained under a H_2 flow for more than 24 hours. After completing the reduction, the catalyst bed temperature was lowered to 310°C and the system put on-stream with Witco-40 mineral oil. A series of experiments were performed (see Table IV-C-4) at 500 psig and 600-620°F, using feed gas mixtures with H_2/CO molar ratios from 3 to over 10. The catalyst activity followed a typical equilibration pattern over the first few days, leveling off at a rate constant of about 1.0×10^{-6} gm-mol/(sec-gm catalyst-atm). This is about two times the value obtained in the pilot plant tests, but only 60 - 70 percent of the activity previously measured with this catalyst.

In September, 1977, more bench scale tests were performed. In the first test, the reduction procedure followed the pilot plant procedure summarized in Table IV-C-5. Surprisingly, the catalyst exhibited an extraordinarily high initial activity of 4.95×10^{-6}. The run was repeated on the next day with essentially the same results (See Table IV-C-6). Because the catalyst activity was much higher than expected, the reactor was by-passed in Run-2b to see if there might be catalyst lodged in the vapor space of the V/L separator. The conversion fell quite rapidly indicating that this was not the case. Two more runs were performed on the third day, both exhibiting high activity. The unit was shut down and the feed gas line examined for catalyst. No catalyst was found. A new charge of catalyst was loaded into the reactor and reduced in an identical manner. The results for this process variable scan are presented in Table IV-C-7. The results for this scan were virtually the

Table IV-C-4

Process Variable Scan: Calsicat Ni-230S[1]/Witco 40 Mineral Oil

Run No.	Pressure (psig)	Temp. (°F)	Feed Gas Flow (liters/hour)	Y^{o}_{CO}[2] (Mole %)	X_{CO} (% Conv.)	$K_{650^{o}}$ (g mole/sec gcat-atm)x10^{6}
1-1a	500	600	630	24.47	85.00	1.91
1-1b	500	600	667	24.47	81.82	1.82
1-2a	500	620	672	25.80	82.47	1.50
1-2b	500	614	689	16.53	85.86	1.42
1-3a	500	613	496	24.90	76.14	0.94
1-3b	500	610	558	12.09	83.69	0.99
1-4a	500	642	548	25.18	76.10	1.07
1-4b	500	612	805	15.73	78.68	1.05
1-4c	500	609	483	9.75	93.70	0.98

[1]Catalyst Loading = 200.0 g $\simeq$ 210 cm^{3}. Nominal particle size is 1.0-2.0 mm.

[2]Balance is H_{2}.

[3]Activation energy used in Arrhenius rate equation is 16000 cal/g mole.

Table IV-C-5 Reduction Schedule: Ni-230S

A - Rigorous	B - Pilot Plant
1) Raise T from 50° to 400°F at 100°F/hr under a N_2 purge (VHSV = 250 HR^{-1})	1) Raise T from 50 - 200°F over 24 hours under a N_2 purge (VHSV = 250 Hr^{-1})
2) Switch to H_2 (VHSV = 1000 Hr^{-1}) and raise T at 100°F/hr to 850°F.	2) Introduce 1 1/2% CO (Balance H_2) at VHSV = 1000 Hr^{-1}
3) Hold for 16 hours at 850°F	3) Raise inlet T at 100°F/hr to 600°F
4) Cool to 650°F at 100°F/hr	4) Raise inlet T at 10°F/hr to 700°F
5) Switch back to N_2 at VHSV + 250 hr^{-1}	5) Lower inlet T at 10°F/hr to 650°F
	6) Switch back to N_2 at VHSV = 250 Hr^{-1}

Table IV-C-6 Process Variable Scan: BSU-6

Calsicat Ni-230S[1] /Witco 40 Mineral Oil

Run No.	Temp. (°F)	Pres. (psig)	Feed gas Flow (l/hr)	Y_{CO}^{o}[2] (%)	Xco (% conv)	$K_{\bar{T}_R}$ (g mole/(sec-gm cat-atm)x10^6)	$K_{650°F}$[3]
6-1a	594	520	735	24.8	99.5	3.20	4.95
6-2a	597	500	690	23.7	99.0	2.90	4.01
6-2b[4]	599	500	750	23.7	12.5	0.09	0.13
6-3a	600	500	890	24.8	97.6	2.90	4.25
6-3b	637	505	1060	24.8	97.8	3.50	3.86

1) Catalyst loading = 200gm $\simeq$ 215 cm^3

2) Balance H_2

3) Activation energy $\simeq$ 16000 cal/g mole

4) Feed gas bypassing reactor.

Table IV-C-7 Process Variable Scan: BSU-7

Calsicat Ni-230S[1]/Witco 40 Mineral Oil

Run No.	Temp. (°F)	Pres. (psig)	Feed gas Flow (l/hr)	Y_{CO}^{o} (2) (%)	X_{CO} (% conv)	K_{T_R} (g mole/(sec-gm cat-atm)x10^6)	$K_{650°F}$ (3)
7-1a	594	500	603	24.6	99.9	3.79	5.71
7-1b	589	500	810	24.6	99.0	3.30	5.18
7-2a	595	500	1030	24.8	92.6	2.37	3.55
7-2b	640	500	1055	24.8	98.3	3.80	4.03
7-3a	636	500	1140	24.1	95.5	3.19	3.38
7-3b[4]	620	500	1280	24.1	6.05	0.07	0.08
7-4a[5]	598	500	755	26.1	1.41	0.009	0.015

1) Catalyst loading = 200 gm≃220 cm^3

2) Balance H_2

3) Activation Energy = 1600 cal/gm mole

4) Feed gas bypassing reactor

5) Reactor empty with gas fed into reactor

same as with the previous run. The Calsicat catalyst exhibited an extremely high activity level. In addition to again bypassing the reactor to check for reaction in the V/L separator (Run 7-3b) catalyst was removed from the reactor and the gas fed in the normal manner. The results for this run (Run 7-4a) confirmed that the catalyst was found exhibiting a high activity level. The rigorous reduction procedure of the previous month's run was repeated with a fourth catalyst load. The results shown on Table IV-C-8 were markedly different from the first bench scale test, yet quite similar to both tests simulating the pilot plant reduction procedure. The results from the first bench scale run were suspect and the catalyst activity level demonstrated in the last three successive bench scale tests is indicative of actual catalyst behavior. The initial activity levels are 5 - 8 times higher than those obtained in the pilot plant runs. This confirms that reduction procedure is not a serious problem but rather the poor gas distribution in the reactor is the major cause of lower catalyst activity. This completed the scheduled bench scale tests with the Calsicat catalyst.

4. Evaluation of INCO Catalysts

In July, 1977, testing began on a new catalyst labeled INCO H, which was specifically prepared for the LPM process. This catalyst is a finely divided (0.25-0.50mm), roughly spherical nickel based material. It is about 3-4 times denser than typical methanation catalysts, with a bulk density of 3.0-3.5 gm/cm^3. Experiments indicated that the material is cost competitive with existing catalysts. In addition, the material has been shown to possess superior physical properties, requires no activation procedure, and is not pyrophoric under normal ambient atmospheric conditions. A variable scan was performed with INCO H in order to check out the operating characteristics prior to full-scale testing in the pilot plant (see Table IV-C-9). The pressure was maintained at 500 psig with temperatures ranging from 580-630^{o}F.

Table IV-C-8 Process Variable Scan: BSU-8

Calsicat Ni-230S[1]/Witco 40 Mineral Oil

Run No.	Temp. (°F)	Pres. (psig)	Feed gas Flow (l/hr)	Y_{CO}^{o} (2) (%)	X_{CO} (% conv)	$K_{\bar{T}_R}$	$K_{650°F}$ (3)
						(g mole/(sec-gm cat-atm)x10^6)	
8-1a	585	500	660	25.6	98.7	2.47	4.24
8-1b	585	500	805	25.6	97.1	2.48	4.24
8-2a	585	500	795	24.2	94.9	2.13	3.37
8-2b	585	500	1045	24.2	90.3	2.20	3.48
8-2c	646	500	1195	24.2	98.7	4.65	4.59
8-3a	643	500	1140	23.8	97.2	3.93	3.69
8-3b	637	500	1375	23.8	93.4	3.40	3.52
8-4a	592	500	830	23.9	91.5	1.86	2.74
8-4b	630	500	790	23.9	98.6	3.10	3.38
8-5a	642	500	900	24.3	98.3	3.27	3.32
8-5b	642	500	1045	24.3	94.9	2.79	2.84
8-5c	642	500	1330	24.3	88.1	2.54	2.58
8-6a	649	500	1115	23.9	95.0	3.04	2.68

1) Catalyst loading = 200 gm $\simeq$ 215 cm^3

2) Balance H_2

3) Activation energy = 1600 cal/g mole

Table IV-C-9

Process Variable Scan: INCO H[1]/Witco 40 Mineral Oil

Run No.	Pressure psig	Temp. °F	Feed Gas Rate liters/hour	Y^{o}_{CO}[2] Mole %	X_{CO} % Conv.	$K_{650^{o}}$[3] (g mole/sec g-cat-atm)x10^{6}
3-1a	500	580	642	26.60	65.66	0.600
1a	500	580	637	26.60	62.88	0.551
1a	500	580	628	26.60	60.65	0.507
1a	500	580	628	26.60	59.44	0.492
3-2a	500	576	586	25.62	62.78	0.509
3-2b	500	590	560	25.62	70.30	0.497
3-3a	500	626	602	25.13	85.49	0.524
3-3b	500	639	530	25.13	89.25	0.458
3-4a	500	622	700	16.49	81.93	0.440
3-4b	500	622	463	16.49	90.40	0.396
3-4c	500	622	506	10.20	89.64	0.287
3-5a	500	624	532	9.95	99.57	0.707
3-5b	500	630	645	25.97	96.29	0.723
3-6a	500	619	459	25.30	95.55	0.681
3-6b	500	620	405	25.30	96.64	0.648

[1]Catalyst Loading = 518.1 g $\simeq$ 150 cm^3. Nominal particle diameter = 0.25-0.50 mm.

[2]Balance is H_2.

[3]Activation energy used in Arrhenius rate equation is 16000 cal/g mole.

Feed gas mixtures with H_2/CO molar ratios of from 3 to 10 were examined. The activity equilibrated fairly rapidly. The activity of 0.5 X 10^{-6} gm mol/(sec-gm catalyst-atm) seemed low only because of the high bulk density of this material. However, based upon a reactivity per unit volume, this would be equivalent to a Calsicat catalyst (bulk density = 0.95 g/cm^3) with a rate constant of about 1.7 X 10^{-6} sm mol/(sec-sm catalyst-atm). The short term decline (Runs 3-4a, b and c) and subsequent sharp rise (Runs 3-5a and b and 3-6a and b) in activity was not fully understood, but possibly equipment related. In any event, the results were sufficiently promising to warrant larger scale testing in the pilot plant. These tests took place during pilot plant Run #3 in late August, 1977.

During the first few hours of pilot plant Run #3, nearly 30 percent of the catalyst bed was carried out of the reactor. A series of fluidization tests were performed in the PDU in order to provide some insight into the start-up problems encountered. At the outset of the PDU experiments it was apparent that the high viscosity of Freezene-100 at ambient conditions caused the catalyst to be smoothly elutriated from the reactor. A particle size distribution of the first material removed from the pilot plant filter is very similar to the as-loaded catalyst, although some classification according to particle size occurred (See Figure IV-C-8). Tests in the PDU indicated that these start-up problems could be alleviated by simply preheating the oil to about 300°F, since the viscosity drops by almost two orders of magnitude over this temperature range (See Table IV-C-10). This procedure was successfully demonstrated at the pilot plant during the second start-up with INCO H.

Having developed a safe start-up procedure, a series of liquid and liquid/gas fluidization runs were performed in order to determine the operating characteristics of this catalyst. The raw data are presented in Table IV-C-11. During the course of the experiments, catalyst was elutriated from the reactor on several occasions due to excessive

FIGURE IV-C-8

PARTICLE SIZE DISTRIBUTION

INCO H

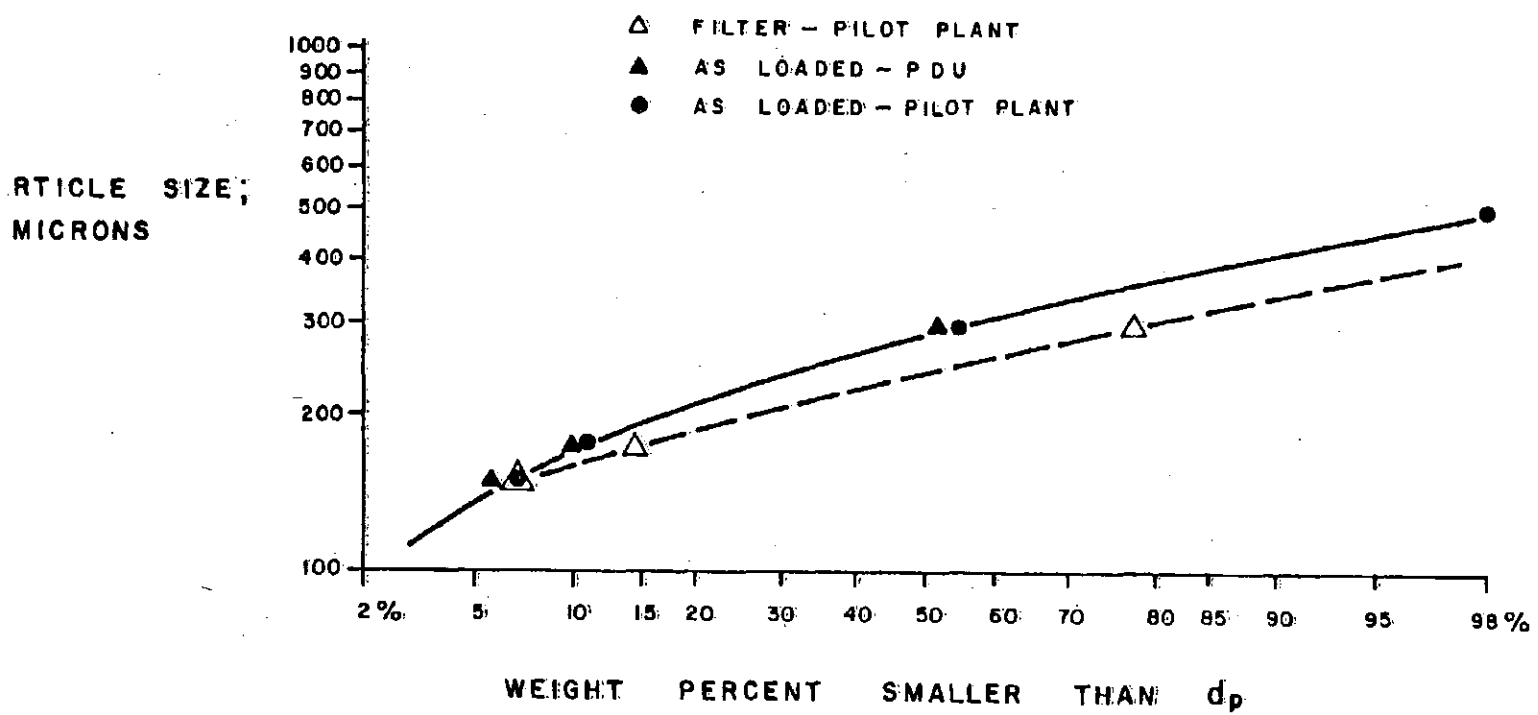


Table IV-C-10 Freezene Viscosity vs. Temperature

Temperature; ^{o}F	Viscosity; cP
0	465.0
100	18.9
200	2.95
300	1.10
400	0.675
500	0.490
550	0.410
600	0.350
650	0.310

Table IV-C-11

INCO H Fluidization[1]

N_2/Freezene 100

Run Number	Temp; °F	Oil Velocity; Ft/Sec	Gas Velocity; Ft/Sec	Settled Bed; Cm.	Fluidized Bed; Cm.
1a	556	0.105	—	72	100
1b	558	0.198	—	72	130
1c	559	0.261	—	60	126
1d	558	0.204	—	60	107
1e	555	0.105	—	60	82
2a	555	0.206	—	60	109
2b	603	0.210	—	60	101
2c	605	0.269	—	60	113
2d	606	0.318	—	58	121
2e	605	0.259	—	56	102
2f	603	0.210	—	56	94
2g	600	0.145	—	56	77
3a	646	0.153	—	56	74
3b	648	0.200	—	56	83
3c	650	0.267	—	56	99
3d	650	0.327	—	56	116
3e	654	0.214	—	56	88
3f	655	0.157	—	56	75
4a	566	0.205	—	56	97
4b	601	0.210	—	56	91
4c	599	0.210	0.0478	56	91
4d	600	0.210	0.0956	55	88
4e	600	0.210	0.143	55	88
4f	599	0.210	0.186	54	88

Table IV-C-11 (Cont'd.)

Run Number	Temp; °F	Oil Velocity; Ft/Sec	Gas Velocity; Ft/Sec	Settled Bed; Cm.	Fluidized Bed; Cm.
4g	602	0.275	0.0478	54	95
4h	601	0.275	0.0980	52	85
4i	601	0.275	0.143	49	79
4j	600	0.275	0.210	47	76
5a	598	0.206	—	47	76
5b	646	0.207	—	47	73
5c	649	0.207	0.055	47	73
5d	650	0.207	0.100	47	74
5e	649	0.207	0.150	47	75
5f	648	0.207	0.198	47	74
5g	649	0.267	0.198	47	77
5h	651	0.267	0.150	47	77
5c	651	0.274	0.100	47	78
5j	651	0.274	0.055	47	80
6a	600	0.207	—	47	77
6b	648	0.207	—	47	71
7a	125	—	0.0263	46	46
7b	125	—	0.0529	46	46
7c	118	—	0.0782	46	46
7d	110	—	0.103	46	46
8a	65	—	0.426	46	46
8b	64	—	0.0772	46	46
8c	64	—	0.0935	46	46

(1) Initial Charge = 15 kg≈4.5 liters

fluidization velocities. The resultant decreases in settled bed height were accounted for during the data correlation. Liquid-only fluidization data are presented in Figure IV-C-9 as a plot of bed expansion ratio versus liquid velocity over the temperature range of 550-650°F. The plots are nearly linear which allows extrapolation to determine the minimum fluidization velocity at these conditions. Interestingly, the minimum fluidization velocity for INCO H catalyst at 650°F is approximately 0.078 ft/sec. while the value previously determined for the Calsicat Ni-230S catalyst was about 0.09 ft/sec. In spite of the extremely different densities and particle sizes, the fluidization velocities are quite similar since the product of density times particle size is nearly constant for the two catalysts.

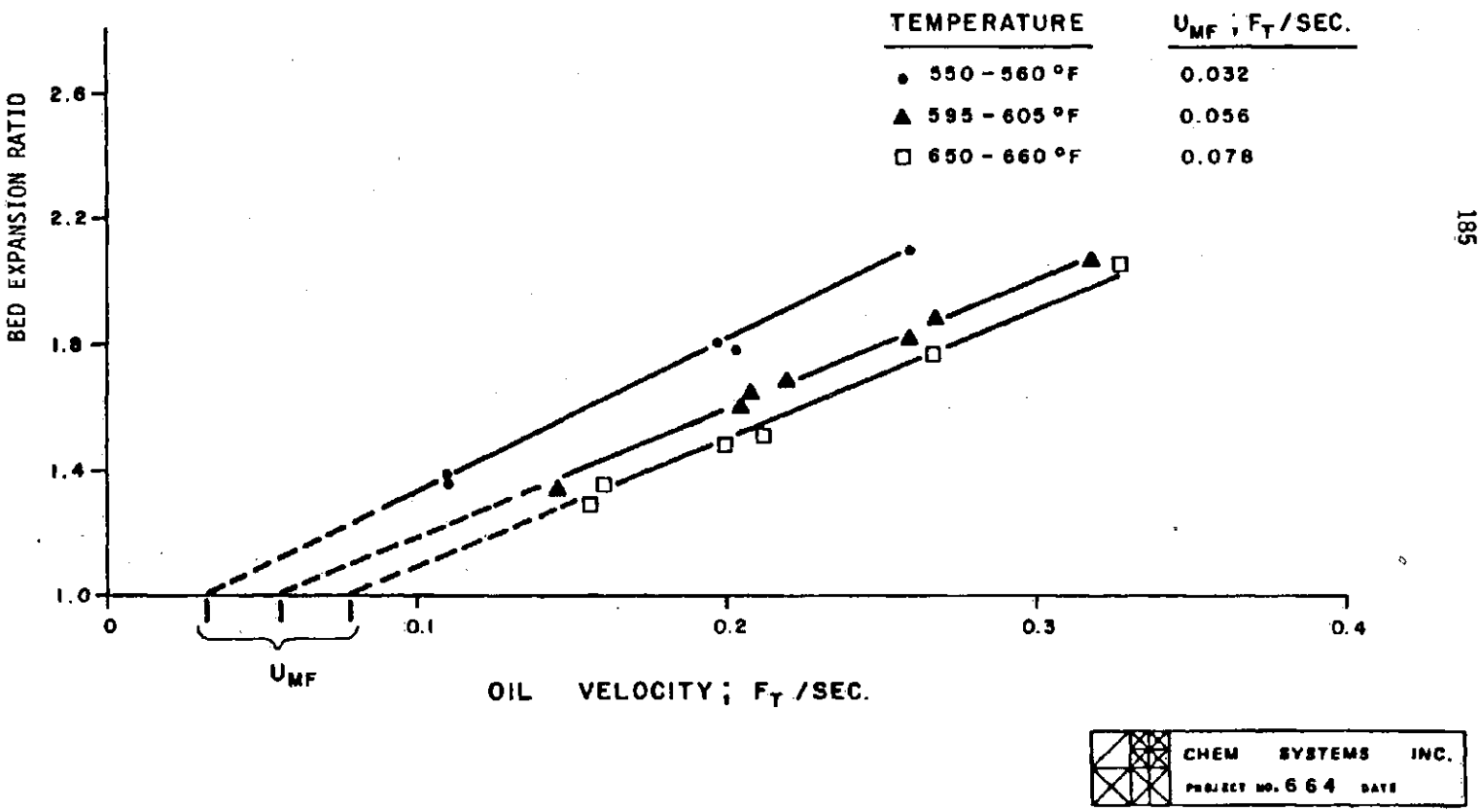
In sharp contrast to the liquid-only case, the liquid/gas fluidization data for the INCO H catalyst differs markedly from the previously obtained results with all the other catalysts. The bed expansion ratio is virtually independent of gas velocity up to gas velocities of more than 0.2 ft/sec. In fact, most of the data show a small contraction in bed height with the addition of gas to the liquid-only fluidized bed. It should be noted that in the pilot plant runs with this catalyst, the addition of gas seemed to carry catalyst out of the reactor. This is contrary to PDU behavior and, evidently, the pilot plant problems are due to poor gas distribution resulting in a "spouting" bed, which causes the catalyst to erupt out of the reactor, as opposed to being smoothly fluidized.

Prior to shutting down and emptying the reactor, several experiments were conducted in which gas was passed through a cold, stagnant liquid filled bed. The purpose of these tests was to see if it would be possible, in the pilot plant, to use a high volume hot gas flow to heat up the reactor without carrying over catalyst. As observed in previous experiments with a bulk liquid flow, the addition of gas to the stagnant bed had virtually no effect on bed expansion or catalyst inventory.

FIGURE IV-C-9

BED EXPANSION VS. LIQUID VELOCITY

INCO H / FREEZENE 100



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

Two modifications of the INCO H catalyst previously tested, INCO D and INCO E, were investigated. All these catalysts have very low surface area and porosity (see Table IV-C-12). The primary differences between the materials are particle size and the method and severity of the activation procedure. All three catalysts are in the active form, requiring no further activation and are essentially non-pyrophoric at ambient conditions. In addition, the materials are very strong, with a high resistance to attrition and dusting. Both catalysts were tested in the bench scale unit over a temperature range of from 550 - 670°F and with feed gas mixtures of 3 - 9 H_2/CO molar ratio. The results for the two variable scans are presented in Tables IV-C-13 (INCO D) and IV-C-14 (INCO E), and compare quite favorably with the value of 0.5 - 0.6 X 10^{-6} for the INCO H catalyst tested in August, 1977. In both cases there were several anomalous areas which can be attributed to peculiar fluidization problems due to the small diameter reactor and to catalyst settling into the reactor inlet area.

5. Further CRG-A Studies

A sample of improved CRG-A 3/32" diameter extrudates was tested in the BSU. This material is from the same production run as a batch sent to the pilot plant. The reduction was carried out with pure H_2 at a maximum temperature of 880°F. The results of the process variable scan are presented in Table IV-C-15. The initial activity levels were extremely high, with a rate constant of 7 - 9 X 10^{-6} gm-mol/(sec-gm catalyst atm). Experiments on the second day gave slightly lower activity levels, 6 X 10^{-6} gm-mol/(sec-gm catalyst-atm). On the third day the pressure drop across the reactor rose to about 60 psi during the start-up. Nevertheless, the activity remained fairly constant. The unit was eventually shut down after the fifth day, at which time the reactor pressure drop was over 100 psi.

Table IV-C-12

Properties of INCO Catalysts

Catalyst	d_p; Micron	bulk density; gm/cc	Surface Area; M^2/gm	Pore Volume: cc/gm
H	200-500	3.3-3.5	2.2	<0.01
D	250-500	3.3-3.5	2.2	<0.01
E	500-1000	3.3-3.5	0.8	<0.01

Table IV-C-13: Process Variable Scan: BSU-4
INCO D [1]/Witco 40 Mineral Oil

Run No.	Temp. (°F)	Pres. (psig)	Feed gas Flow (l/hr)	Y_{CO}[2] (%)	X_{CO} (% conv)	K_{T_R}	$K_{650°F}$[3] (g mole/(sec-gm cat-atm)x10^6)
4-1a	583	510	545	24.2	79.6	0.32	0.70
4-1b	581	510	480	24.2	72.6	0.23	0.52
4-2a	614	510	590	25.5	96.8	0.76	1.20
4-2b	613	510	605	16.3	97.3	1.08	0.98
4-2c	615	510	680	16.3	95.9	1.08	0.96
4-3a	624	510	650	25.0	94.5	0.70	0.95
4-3b	624	510	515	25.0	96.4	0.64	0.87
4-3c	616	510	515	17.1	97.4	0.92	0.86
4-4a	626	510	455	16.9	98.8	0.99	0.80
4-4b	626	510	760	16.9	94.9	1.12	0.91
4-4c	626	510	1030	16.9	91.7	1.26	1.02
4-5a	626	510	535	25.9	97.4	0.72	1.01
4-5b	626	510	730	13.1	93.4	1.08	0.68
4-5c	626	510	810	17.0	96.4	1.32	1.09
4-6a	626	510	580	26.0	96.1	0.70	0.98
4-6b	644	520	515	26.0	99.5	0.99	1.12
4-7a	630	510	655	17.9	94.4	0.91	0.75
4-7b	663	500	1215	17.9	98.2	2.37	1.32
4-7c	662	500	910	10.7	99.9	3.01	0.95

1) Catalyst loading = 460 gm$\simeq$130 cm^3, dp = 250-500μ

2) Balance H_2

3) Activation energy = 16000cal/g mole

Table IV-C-14: Process Variable Scan: BSU-5
INCO E[1]/Witco 40 Mineral Oil

Run No	Temp. (°F)	Pres. (psig)	Q (l/hr)	Y_{CO}^{o}[2] (%)	X_{CO} (% conv)	K_{T_R}	$K_{650°F}$[3]
						(g mole/(sec-gm cat-atm)x10^6)	
5-1a	622	500	610	25.8	79.6	0.37	0.52
5-1b	622	500	525	25.8	86.3	0.41	0.56
5-2a	626	500	270	25.1	97.6	0.79	1.05
5-2b	658	505	230	25.1	99.6	1.19	1.08
5-2c	662	510	275	25.1	99.1	1.16	1.01
5-3a	623	505	565	24.7	88.7	0.48	0.66
5-3b	635	500	500	24.7	91.7	0.48	0.57
5-4a	647	505	570	24.8	92.1	0.56	0.58
5-4b	650	500	500	24.8	94.0	0.55	0.55
5-5a	658	500	540	24.7	97.2	0.75	0.68
5-5b	617	500	450	24.7	82.3	0.31	0.46
5-5c	575	505	345	24.7	61.7	0.23	0.60
5-6a	615	975	1030	24.8	85.7	0.40	0.60
5-6b	654	975	1030	24.8	96.4	0.68	0.65

1 Catalyst loading = 460 gm ≃ 130 cm^3, dp = 500-100 μ

2 Balance H_2

3 Activation Energy = 16000 cal/g mole

Table IV-C-15: Process Variable Scan: BSU Run #9
CRG-A[1]/WITCO 40

Run No.	Temp. (°F)	Pressure (psig)	Feed Gas Flow (liters/hr)	y^{o}_{CO}[2] (%)	CO Conversion (%)	K_{T_R}	K_{650^oF}[3] (gm moles/(sec-gm cat-atm)x10^6)
9-1a	600	500	1220	25.2	99.2	5.10	8.99
9-1b	600	500	1360	25.2	97.4	4.31	7.60
9-2a	600	500	1325	25.1	95.1	3.47	6.07
9-2b	600	500	1535	25.1	91.8	3.34	5.85
9-2c	646	500	1955	25.1	98.2	6.87	7.28
9-3a[4]	579	500	945	23.5	96.1	2.83	6.35
9-3b	636	510	1325	23.5	99.5	6.37	6.93
9-3c	650	510	1850	23.5	98.8	7.40	6.81
9-4a[5]	646	505	1520	25.3	98.6	5.60	5.99
9-5a[6]	597	510	1185	25.3	90.1	2.34	4.67

(1) 3/32" Ø extrudates; Catalyst loading = 200 gm≃180 - 190 cm^3
(2) Balance H_2
(3) Activation energy - 16,000 cal/gm mole
(4) Reactor P≃20 psi
(5) Reactor P≃60 psi
(6) Reactor P≃100 psi

When the reactor was opened, a 6-inch long plug was found in the upper section. In the past, similar reactor plugging has occurred with this catalyst during start-up. At that time, it was discovered that, if the unit were started up and run continuously, catalyst agglomeration would occur. This problem is related entirely to method of start-up and shut-down. A new batch of catalyst was loaded, reduced, and a continuous process variable scan was performed over a 30-hour period. The results are presented in Table IV-C-16. The base case point was repeated several times (Figure IV-C-10). After correcting the apparent activity to the final equilibrated level, the data were correlated on an Arrhenius plot shown in Figure IV-C-11 and an activation energy of 18,750 cal/gm mol calculated. This value is higher than typical, leading to an equilibrated activity level at 650°F of 7.4 X 10^{-6} gm-mol/sec-gm catalyst-atm). This was 2 - 4 times more active than any other catalyst candidate tested.

The PDU was loaded with the same Grace CRG-A catalyst tested in the bench scale unit. The incinerator and CO monitor installations were completed and the unit was ready for startup in early November, 1977.

The catalyst was reduced with hydrogen at 800°F as opposed to the 890°F recommended by the manufacturer due to problems with the temperature control system. Since under ordinary circumstances, even 800°F is sufficient to reduce a methanation catalyst, the planned process variable scan was continued. The results for PDU Run #10 are presented in Table IV-C-17. The initial and equilibrated activity values of 3 X 10^{-6} and 2 X 10^{-6} gm-mol/(sec-gm catalyst-atm), respectively, are only one-third the values obtained in the previous bench scale tests, but comparable to results obtained with other catalysts in the PDU. Never before having experienced such a wide discrepancy between BSU and PDU results, it was suspected that the difference in reduction temperature was responsible. This was substantially verified by representatives of W. R. Grace who indicated that their records for vapor

Table IV-C-16. Process Variable Scan: BSU Run #10

CRG-A[1]/WITCO 40

Run No.	Hours on Stream	Temp. (°F)	Press. (psig)	Feed Gas Flow (liters/hr)	y^{o}_{CO} [2] (%)	CO Conv. (%)	K_{T_R} (gm moles/(sec-gm cat-atm)x10^6)	$f(t)\ K_{650°F}$ [3] (gm moles/(sec-gm cat-atm)x10^6)
10-1a	2	590	500	1420	24.3	99.02	5.90	2.98
10-1a	3	590	500	1445	24.3	98.91	5.85	3.15
10-1b	4	590	500	5130	24.3	98.14	5.47	3.08
10-1b	5	590	500	1525	24.3	98.94	5.32	3.15
10-1c	6	590	500	1685	24.3	95.70	4.75	2.93
10-1c	7	590	500	1830	24.3	95.21	4.99	3.22
10-1d	10	615	500	1900	24.3	96.08	5.53	3.99
10-1e	11	615	500	2185	24.3	93.69	5.43	4.05
10-1e	12	615	500	2210	24.3	93.73	5.50	4.24
10-1f	14	642	500	2320	24.3	98.91	9.41	7.68
10-1f	15	642	500	2260	24.3	97.77	7.72	6.47
10-1g	16	642	500	2010	24.3	98.63	7.75	6.61
10-1g	17	642	500	1960	24.3	98.67	7.61	6.61
10-1h	19	594	500	1360	24.3	94.52	3.55	3.18
10-1h	20	594	500	1355	24.3	93.24	3.28	2.98
10-1i	21	594	500	1635	24.3	90.77	3.50	3.23
10-1i	22	594	500	1590	24.3	90.25	3.32	3.10
10-1j	23	617	500	1855	24.3	96.18	5.44	5.12
10-1j	24	617	500	1775	24.3	96.20	5.21	4.92
10-1k	25	590	500	1310	24.3	92.79	3.09	2.93
10-1k	26	590	500	1325	24.3	92.70	3.11	2.97
10-1l	27	590	500	1170	24.3	96.08	3.40	3.24
10-1l	28	590	500	1155	24.3	96.00	3.34	3.18

(1) 3/32" Ø extrudates; Catalyst loading = 200 gm≃180 - 190 cm^3

(2) Balance H_2

(3) Activation energy = 18,750 cal/gm mole

FIGURE IV-C-10

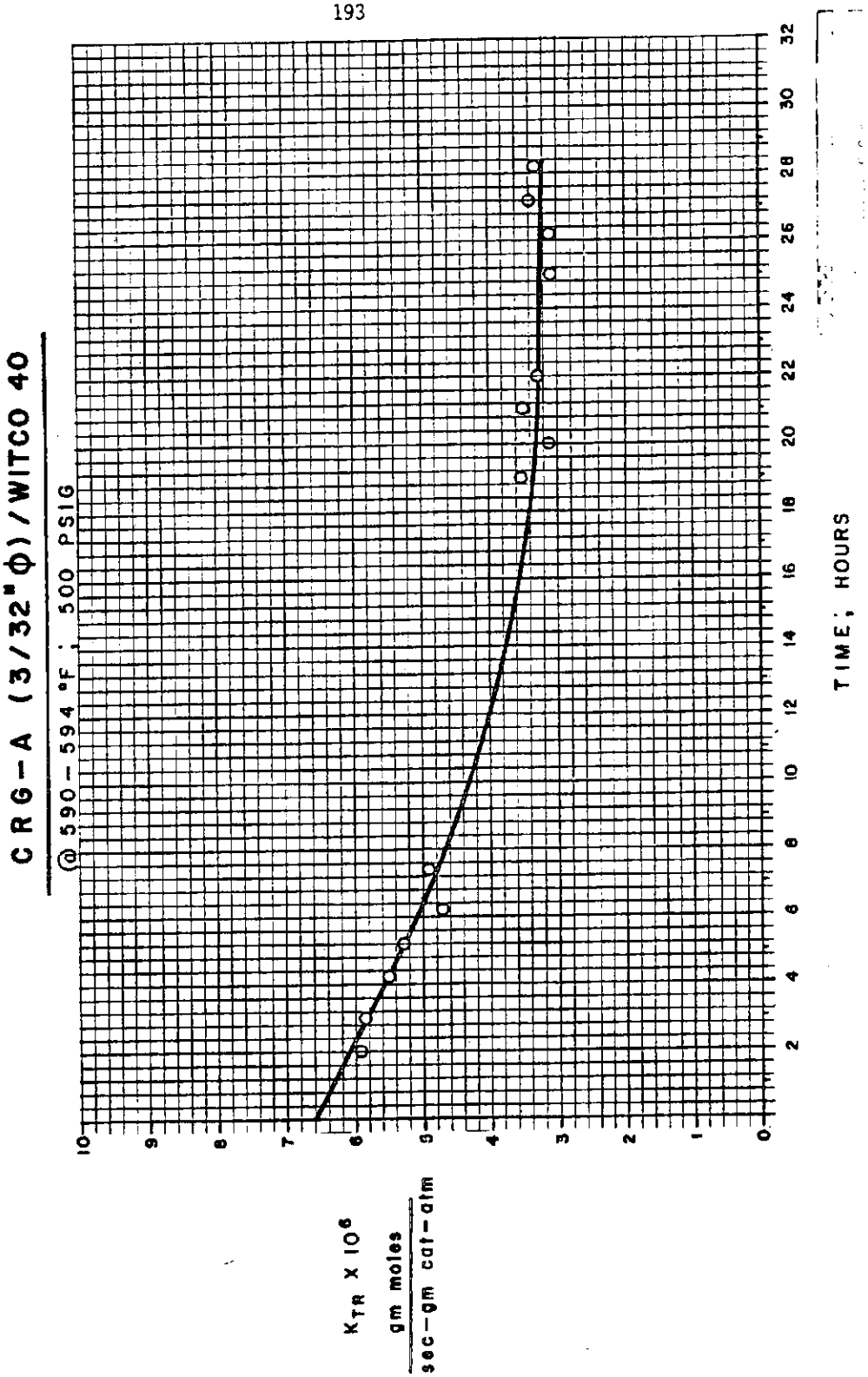
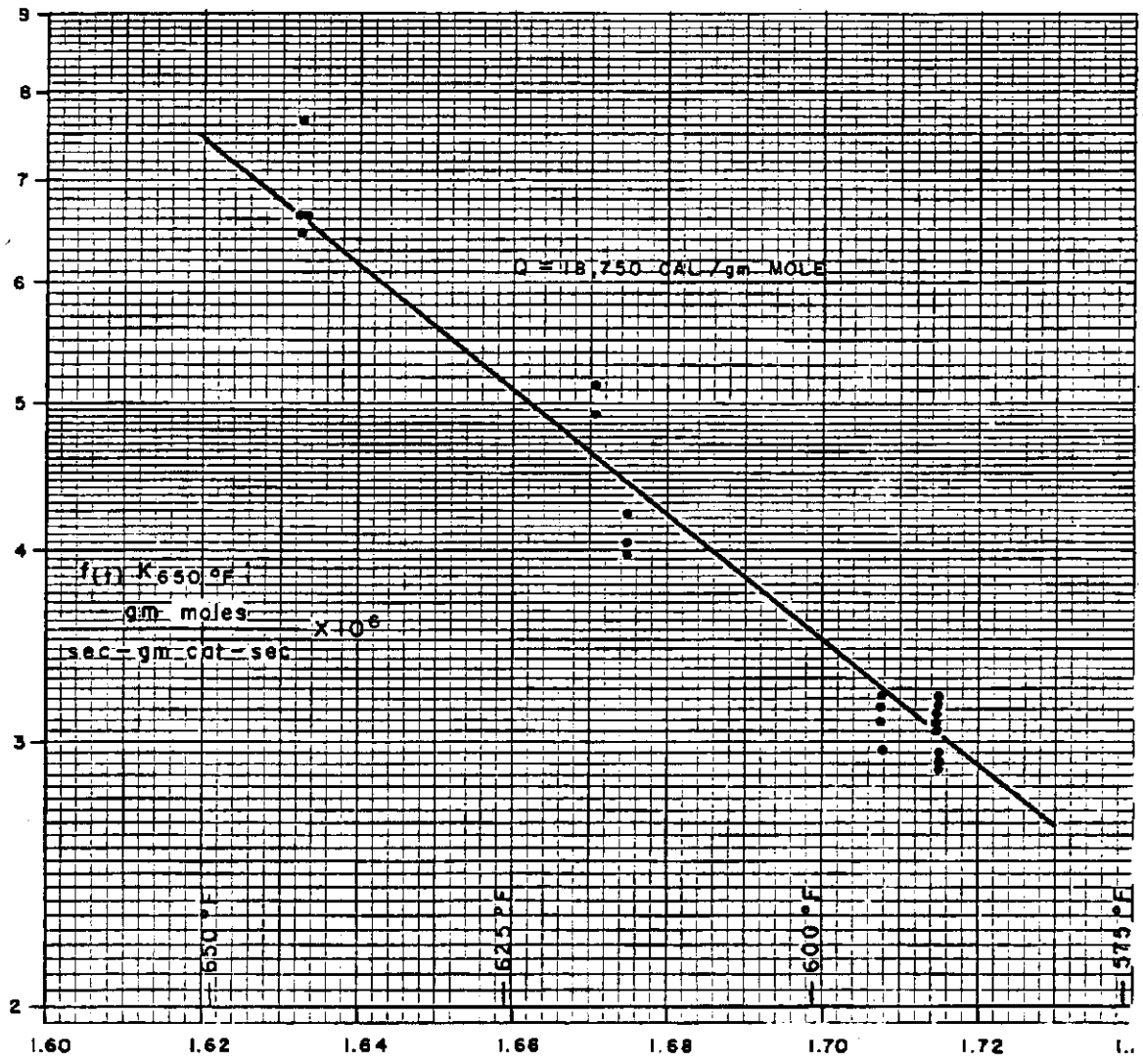


FIGURE IV-C-11

ARRENIUS PLOT - BSU Run #10

CRG-A (3/32" ϕ) / WITCO 40

BENCH SCALE UNIT



CHEM SYSTEMS INC.
PROJECT NO. 6 6 4 DATE

Table IV-C-17: Process Variable Scan: PDU Run #10
Grace CRG-A (3/32" Ø Extrudates) (1)/Freezene 100

Run. No.	Temp. (°F)	Pressure (psig)	Feed Gas Flow (2) (SCFH)	CO Conversion (%)	$K_{\bar{T}_R}$ (gm moles/sec-gm cat-atm)x10	$K_{650°F}$ (3
10-1a	650	500	585	99.4	2.91	2.91
10-1b	650	500	1005	94.5	2.88	2.88
10-2a	650	500	1040	93.1	2.76	2.76
10-2b	650	500	1450	85.8	2.80	2.80
10-3a	650	500	405	94.0	1.12	1.90
10-3b	650	500	495	98.6	2.09	2.09
10-3c	650	500	915	91.7	2.24	2.24
10-3d	675	500	1040	95.0	3.08	2.42
10-4a	550	500	380	84.3	0.70	2.11
10-4b	600	500	425	94.7	1.23	2.08
10-4c	650	500	505	98.7	2.19	2.19
10-4d	675	500	515	99.3	2.48	1.95
10-4e	675	500	995	93.4	2.67	2.10
10-5a	650	500	915	88.3	1.94	1.94

(1) Catalyst loading = 11.0 lbs.

(2) Nominal composition = 75 % H_2, 25 % CO

(3) Activation energy $\simeq$ 13,600 cal/gm-mole

phase reaction experiments show more than a factor of two (2) difference in activity attributable to this difference in reduction temperature. It should be noted that the activity level for this catalyst was still greater than the original design basis. More importantly, it is the first extrudate form that has possessed sufficient physical strength to withstand the liquid phase reaction conditions. The economic benefits of an extrudate versus tablet form are significant, amounting to several dollars per pound of catalyst.

PDU Run #10 lasted approximately 60 hours and was terminated upon successful completion of the planned process variable scan. Two filter elements plugged and were changed during the first day of operation and two additional elements plugged with catalyst fines during the remainder of the week of operation.

A second charge of Grace CRG-A extrudates were loaded into the PDU and reduced. Since the temperature controller was repaired, maximum reduction temperatures of 890^{o}F were achieved. The reactor was put on-stream in the normal manner. However, within the first hour of operation, the initial process oil filter plugged. The second filter plugged shortly thereafter.

While attempting to maintain process oil flow, the reactor also plugged. PDU Run #11 was terminated and the unit was shut down, cooled and vented. Examination of the catalyst revealed physical degradation of the extrudates. It seemed that the higher reduction temperature was responsible for an unusual reduction in catalyst particle physical strength, though this was not readily apparent in the previous BSU tests.

After thoroughly cleaning the system, another catalyst charge was loaded and reduced, this time at maximum reduction temperature of 850^{o}F. Again, rapid plugging of the process oil filters was experienced and PDU Run #12 was terminated. PDU Run #13 was similarly aborted due to rapid catalyst attrition.

The Process Development Unit experimental work with Grace 3/32" diameter extrudates was completely reviewed. This included the data from PDU Run #10 as well as PDU Runs #14 and #15, to be discussed below. Runs #11, #12, and #13 were all aborted shortly after start-up because of rapid catalyst breakup attributed to excessive reduction temperatures. While the 850-890°F reduction temperature used in these runs is within the recommended levels for this catalyst in vapor phase methanation, it results in particle strengths that are too low for a liquid phase system. However, all runs that employed a reduction temperature of higher than 800°F resulted in a stable operation with minimal catalyst loss. It is true, however, that continued and sometimes rapid plugging of the process filters occurred. Examination of the filter elements showed only a light surface deposit of catalyst dust, and the bulk of the filter internals appeared to be unused. A representative of Facet, Inc., the filter manufacturer, later explained that the glass yarn used in the current filter element appears to be extremely fluffy, resulting in a very tight, close weave. This, in effect, gives a significantly lower particle size cut point (less than 10 microns instead of the intended 50-100 microns), resulting in very rapid blinding of the filter element.

When the actual reaction results were reviewed, consistently large (20-30 percent) deviations from the calculated mass balance of the systems were found. The stream flow values were obtained from a series of integral orifice meter transmitters. The feed system was monitored at the feed gas compressor and then again at the reactor inlet. Readings at these two valves were generally within 5 percent of each other. The effluent stream was monitored with a third orifice meter, just upstream of the pressure control valve. Here, the pressure control response resulted in a fairly wide flow band ($\pm$ 20 - 30 percent) that was difficult to read accurately. However, this problem could not by itself account for such a consistent and large discrepancy in flows. At the end of Run #15, the zero and span calibrations of all the orifice meters were checked. The reading at the feed orifice was found to be only about 3 percent too low, and the compressor and effluent orifices were at their calibration value.

It is possible that the effluent gas stream contains small oil droplets that markedly increase the effective gas density. Although only 2 percent by volume of oil could account for the 30 percent flow error, such an oil loss is more than four times greater than that actually experienced. Thus, since the flow discrepancy was not resolved, all reactivity values were calculated using the lower flow value for the compressor orifice.

Each run involved reaction experiments carried out over four to five days. Because a weekend usually intervened, the total run spanned seven or eight calendar days. In the case of Run #14, an intervening snowstorm caused nearly a week delay in a gas delivery, so that the catalyst remained in the reactor for twelve days. Between Run #14 and Run #15, the test design bubble cap distributor was installed in the bottom of the PDU reactor. The design incorporated an integral ball-check to prevent solids loss through the liquid-gas inlet line where gas and liquid flows are stopped.

The major events of PDU Run #14 are summarized in Table IV-C-18 and the results are summarized in Table IV-C-19. The major events of PDU Run #15 are summarized in Table IV-C-20 and the results are listed in Table IV-C-21. Catalyst activity as a function of time is plotted in Figures IV-C-12 and IV-C-13 for Runs #14 and #15, respectively.

In each run, the initial activity level was $2.45 \pm 0.20 \times 10^{-6}$ gm-mol/(sec-atm-gm catalyst). This gradually declined to an equilibrium value of $1.70 \pm 0.10 \times 10^{-6}$ gm-mol/(sec-atm-gm catalyst). Little, if any, change was measured for settled bed height throughout the runs. When the reactor was emptied at the end of each run, the catalyst was visually examined. In all cases, there was evidence of some particle breakage. This finding was expected, however, because the reactor density profiles had shown a diffuse catalyst bed interface after several days in the reactor. On the basis of these results, the Grace catalyst

TABLE IV-C-18

SUMMARY OF EVENTS FOR PDU RUN #14

Hours on Stream	Date	Accumulated Reaction Time	Event
0	1/13/78	0	Reactor loaded with 11.0 lb Grace 3/32" Ø CRG-A extrudates. Heated with N_2 to 400°F. Maintained over weekend.
0	1/16/78	0	Switched to H_2 and heated at 100°F per hour to 800°F. Dry settled bed height is 77.5 cm.
0	1/17/78	0	H_2 flow stopped. Reactor pressurized to 600 psig and isolated. System pressurized to 100 psig and liquid flow initiated. System heated to 650°F and pressure raised to 500 psig. First oil filter plugged rapidly. Inner seal of process oil pump temporarily failed, flooding vessels with excess oil. Problem corrected itself.
0	1/17/78	0	System at 650°F and 500 psig. Process gas flow started (830 SCFH). Second filter put on stream. Leak at reactor inlet caught fire. It was extinguished and the fitting tightened. Fluidized bed height is 110 cm.
8	1/17/78	8	Process gas stopped. Oil flow was diverted to reactor bypass and reactor inlet was closed. Reactor was maintained at 650°F while the rest of the system was cooled to 400°F and shut down for the night.
21	1/18/78	8	Started to pressurize and heat up PDU. Settled bed height is 73 cm.

TABLE IV-C-18 (Continued)

SUMMARY OF EVENTS FOR PDU RUN #14

Hours on Stream	Date	Accumulated Reaction Time	Event
23	1/18/78	9	PDU at 650°F and 500 psig. Compressor started and set at base case flow (805 SCFH).
31	1/18/78	16	Process gas stopped. Followed standard shutdown procedure. Settled bed height is 76 cm.
45	1/19/78	16	Dismantled upper filter and removed cartridge; very little catalyst accumulation. Outer covering split, probably due to high ΔP. Reassembled with a new element. Settled bed height is 76 cm.
47.5	1/19/78	16.5	PDU at process conditions of 650°F, 500 psig and a compressor flow of 790 SCFH. Fluidized bed height is 120 cm.
56	1/19/78	25	Shut down unit. Settled bed height is 76 cm.
141	1/23/78	23	Settled be height is 78 cm. Started unit heat-up.
142.5	1/23/78	24.5	Unit at process conditions of 650°F, 500 psig and a compressor flow of 785 SCFH.
146.5	1/23/78	28.5	Raised compressor flow to 1005 SCFH.
149	1/23/78	31	Lowered compressor flow to 490 SCFH.
152.5	1/23/78	34.5	Shut down unit. Circulating oil sample contains considerable solids. Suspect oil is internally bypassing filter element.

TABLE IV-C-18 (Continued)

SUMMARY OF EVENTS FOR PDU RUN #14

Hours on Stream	Date	Accumulated Reaction Time	Event
164.5	1/24/78	34.5	Started up unit with flow in filter bypass. Heating up to 650°F at 500 psig. Settled bed height is 76 cm.
165.5	1/24/78	34.5	Put new filter onstream. Filter ΔP rose rapidly from 2 psi to 15 psi within a matter of minutes. This resulted in low carrier flow. Switched to other filter. Pressure drop was same (4.1 psi) as on previous day, confirming fact that oil flow is internally bypassing filter element.
167	1/24/78	34.5	Unit at process conditions. Attempted to switch oil flow to reactor inlet. Discovered that reactor inlet is plugged. Run terminated.
167	1/25/78	34.5	Catalyst removed from reactor. Reactor inlet tube contained pieces of solids. About 80 percent of the catalyst particles showed only slight signs of wear such as rounding of corners. The remaining 20 percent evidenced substantial particle breakage. These smaller particles are probably the cause of the diffuse catalyst bed height measurement.

Table IV-C-19 LPM PDU Run # 14 RESULTS

Hour	1	2	4	6	8	27
Accumulated Reaction Time (Hrs)	1	2	4	6	8	27
Feed Gas:						
H_2/CO Ratio	3.28	3.28	3.28	3.28	3.28	3.18
% H_2	76.64	76.64	76.64	76.64	76.64	76.06
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	23.36	23.36	23.36	23.36	23.36	23.94
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	4,745	4,745	4,745	4,745	4,745	4,600
Oil Flow Rate: GPM/Ft^2	88	88	88	88	88	91
Temperature (°F)	650	650	650	650	650	650
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	23.45	22.27	23.36	22.50	23.38	30.03
% N_2	—	—	—	—	—	—
% CH_4	65.19	67.60	66.13	66.80	66.28	59.25
% CO	2.77	3.16	3.49	3.86	4.02	5.88
% CO_2	8.59	6.98	7.03	6.84	6.32	4.84
% C_2^+	—	—	—	—	—	—
MW	15.49	15.25	15.15	15.26	15.01	13.89
SCFH	—	—	—	—	—	—
CO Conversion (%)	96.38	95.94	95.45	95.02	94.75	91.60
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	88.36	96.64	90.40	90.71	91.30	92.45
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	2.66	2.56	2.47	2.40	2.36	2.06
$K_{650°F}$ (x 10^6)	2.66	2.56	2.47	2.40	2.36	2.06
Run Number	1a	1b	1c	1d	1e	2a
Bed Height (FT)	110 cm.	—	—	—	—	119 cm.

Table IV-C-19 LPM PDU Run # 14 RESULTS (continued)

Hour	29	31	51	53	56	146
Accumulated Reaction Time (Hrs)	14	16	20	22	25	28
Feed Gas:						
H_2/CO Ratio	3.18	3.18	2.95	2.95	2.95	2.94
% H_2	76.06	76.06	74.66	74.66	74.66	74.74
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	23.94	23.94	25.34	25.34	25.34	25.26
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	4,600	4,600	4,515	5,860	2,660	4,490
Oil Flow Rate: GPM/Ft^2	89	90	91	91	91	91
Temperature (°F)	600	625	650	650	650	650
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	48.62	34.14	29.76	37.23	16.02	34.31
% N_2	—	—	—	—	—	—
% CH_4	37.13	54.19	59.03	49.71	76.31	53.35
% CO	11.34	8.11	6.59	9.42	0.84	8.06
% CO_2	1.93	3.56	4.62	3.64	6.81	4.29
% C_2^+	—	—	—	—	—	—
MW	11.07	13.22	13.95	12.97	15.83	13.39
SCFH	—	—	—	—	—	—
CO Conversion (%)	77.51	87.68	90.62	84.99	99.00	87.73
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4^2 Selectivity (%)	95.04	93.83	92.75	93.17	91.80	92.56
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	1.25	1.64	1.88	1.93	1.90	1.68
$K_{650°F}$ ($\times 10^6$)	1.98	2.12	1.88	1.93	1.90	1.68
Run Number	2b	2c	3a	3b	3c	4a
Bed Height (FT)	120 cm.	121 cm.	120 cm.	124 cm.	110 cm.	—

Table IV-C-19: LPM PDU Run # 14 RESULTS (continued)

Hour	149	167				
Accumulated Reaction Time (Hrs)	31	35				
Feed Gas:						
H_2/CO Ratio	2.94	R				
% H_2	74.74	U				
% N_2	—	N				
% CH_4	—	T				
% CO	25.26	E				
% CO_2	—	R				
% C_2^+	—	M				
VHSV (Hr^{-1})	4,490	I				
Oil Flow Rate:		N				
GPM/Ft^2	91	A				
Temperature (°F)	645	T				
Pressure (psig)	500	E				
Product Gas:		D				
% H_2	40.11					
% N_2	—					
% CH_4	44.50					
% CO	11.91					
% CO_2	3.23					
% C_2^+	—					
MW	12.82					
SCFH	—					
CO Conversion (%)	79.33					
CO_2 Conversion (%)	—					
CH_4 Selectivity (%)	92.73					
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	1.63					
$K_{650°F}$ (x 10^6)	1.68					
Run Number	4b					
Bed Height (FT)	—					

TABLE IV-C-20

SUMMARY OF EVENTS FOR PDU RUN #15

Hours on Stream	Date	Accumulated Reaction Time	Event
-	1/31/78	-	Reactor loaded with 11.0 lbs Grace 3/32" Ø CRG-A extrudates. Heated with N_2 to 400°F. Standard H_2 reduction at 800°F. Dry settled bed height is 69 cm.
0	2/02/78	0	During PDU start-up, found a plug in reactor bypass line. Removed purge meter and replaced with a section of tube. Started feed gas.
3	2/02/78	3	Unit at process conditions of 500 psig, 650°F and a compressor flow of 795 SCFH.
6	2/02/78	6	Raised compressor flow to 1000 SCFH.
7	2/02/78	6	Feed gas supply insufficient to continue point. Filter will be changed on next start-up. Shut down unit for the night.
22	2/03/78	6	Replace filter element. Remove new plug in reactor bypass line. Settled bed height is 78 cm.
24	2/03/78	6	Start to heat and pressurize PDU.
26	2/03/78	6	Unit at process conditions of 500 psig, 650°F, and a compressor flow of 425 SCFH. Filter $\triangle P$ = 3.0 psi.
27	2/03/78	7	Filter plugged very rapidly. Switched to clean filter.

TABLE IV-C-20 (Continued)

SUMMARY OF EVENTS FOR PDU RUN #15

Hours on Stream	Date	Accumulated Reaction Time	Event
28	2/03/78	8	Switched to cylinder bank.
31	2/03/78	11	Shut down unit for the night. No feed gas left in trailer or cylinder bank.
43	2/04/78	11	Unit idled due to snow storm and delayed feed gas trailer delivery. Replaced plugged filters and performed other maintenance tasks. Settled bed height is 77 cm.
190	2/10/78	11	Start to heat and pressurize PDU.
191	2/10/78	11	Leak in reactor bypass line. Flow stopped and line section depressurized in order to repair.
193	2/10/78	11	System at process conditions of 500 psi, 650^{o}F and a compressor flow of 805 SCFH.
194.5	2/10/78	12/5	Filter plugged. Unable to maintain liquid flow. Switched to bottom filter.
196.5	2/10/78	14.5	Filter plugged. Unable maintain flow. Switched to top filter.
200	2/13/78	18	Filter plugged. Shut down unit. Seems to be a plug forming in flow system

TABLE IV-C-20 (Continued)

SUMMARY OF EVENTS FOR PDU RUN #15

Hours on Stream	Date	Accumulated Reaction Time	Event
261	2/13/78	18	Changed both filters. Found several plugs in the liquid lines from pumps through the heaters. Cleaned these lines. Pulsed pump on and off. Plug seemed to clear. Settled bed height is 79 cm.
268	2/13/78	18	Started to heat and pressurize PDU.
269	2/13/78	19	PDU at process conditions of 500 psi, 650°F, and a compressor flow of 795 SCFH.
269.5	2/13/78	19.5	Filter plugged.
270	2/13/78	20	Changed to bottom filter.
270.5	2/13/78	20.5	New filter already plugged. Shut down unit to inspect heaters.
	2/14/78		Up-flow heater element found to be totally coked and wedged into heater body. Removed for repair and replaced with the spare element. Catalyst emptied from reactor and inspected. Some breakage is evident. The entire liquid flow loop was cleaned in order to remove solids resulting from the coked heaters.

Table IV-C-21 LPM PDU Run # 15 RESULTS

Hour	4	6	28	30	196	197
Accumulated Reaction Time (Hrs)	4	6	8	10	14	15
Feed Gas:						
H_2/CO Ratio	2.86	2.86	2.90	2.90	3.05	3.05
% H_2	74.10	74.10	74.37	74.37	76.07	76.07
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	25.90	25.90	25.63	25.63	23.93	23.93
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	4,540	4,540	2,430	2,430	4,600	4,600
Oil Flow Rate: GPM/Ft^2	97	97	97	97	97	97
Temperature (°F)	648	650	649	599	645	647
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	27.50	27.69	21.07	30.50	37.92	36.94
% N_2	—	—	—	—	—	—
% CH_4	62.25	61.89	70.66	57.71	49.47	50.46
% CO	3.90	4.07	1.48	5.05	8.59	8.74
% CO_2	6.36	6.34	6.79	6.74	4.02	3.86
% C_2^+	—	—	—	—	—	—
MW	14.43	14.42	15.16	14.26	12.88	12.99
SCFH	—	—	—	—	—	—
CO Conversion (%)	94.61	94.37	98.12	92.73	86.16	86.14
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4^2 Selectivity (%)	90.75	90.71	91.24	89.53	92.49	92.90
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	2.40	2.37	1.88	1.13	1.56	1.57
$K_{650°F}$ ($\times 10^6$)	2.44	2.37	1.90	1.93	1.62	1.60
Run Number	1a	1b	2a	2b	3a	3b
Bed Height (FT)	116 cm.	114 cm.	104 cm.	104 cm.	110 cm.	—

Table IV-C-21 LPM PDU Run # 15 RESULTS (continued)

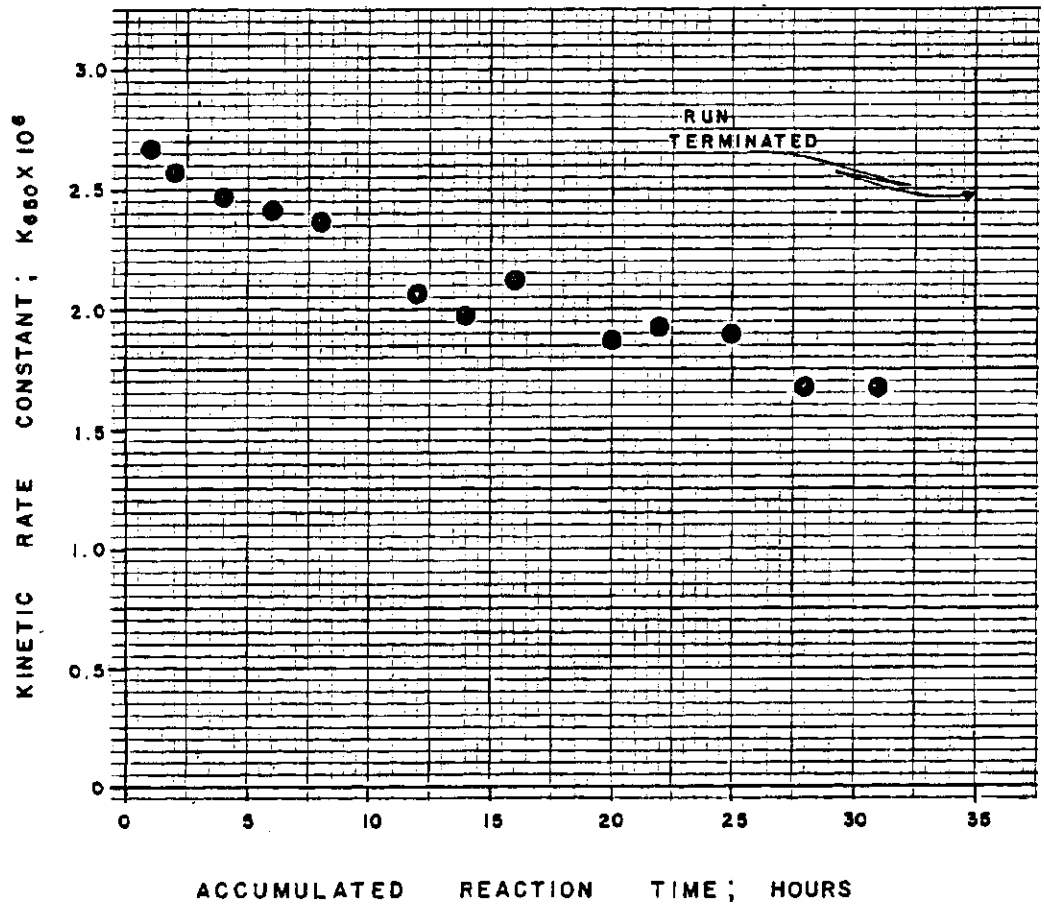
Hour	200	270	270.5			
Accumulated Reaction Time (Hrs)	18	20	20.5			
Feed Gas:			RUN TERMINATED			
H_2/CO Ratio	3.05	3.05				
% H_2	76.07	75.32				
% N_2	—	—				
% CH_4	—	—				
% CO	23.93	24.68				
% CO_2	—	—				
% C_2^+	—	—				
VHSV (Hr^{-1})	4,600	4,540				
Oil Flow Rate: GPM/Ft^2	97	97				
Temperature (°F)	646	645				
Pressure (psig)	500	500				
Product Gas:						
% H_2	36.34	42.38				
% N_2	—	—				
% CH_4	50.96	45.90				
% CO	8.62	8.42				
% CO_2	4.07	3.29				
% C_2^+	—	—				
MW	13.11	12.03				
SCFH	—	—				
CO Conversion (%)	86.45	85.38				
CO_2 Conversion (%)	—	—				
CH_4 Selectivity (%)	92.66	93.31				
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	1.59	1.49				
$K_{650°F}$ (x 10^6)	1.63	1.58				
Run Number	3c	4a				
Bed Height (FT)	—	—				

FIGURE IV-C-12

CATALYST ACTIVITY VS. REACTION TIME

LPM PDU RUN #14

GRACE CRG-A EXTRUDATES / FREEZENE-100



CHEM SYSTEMS INC.

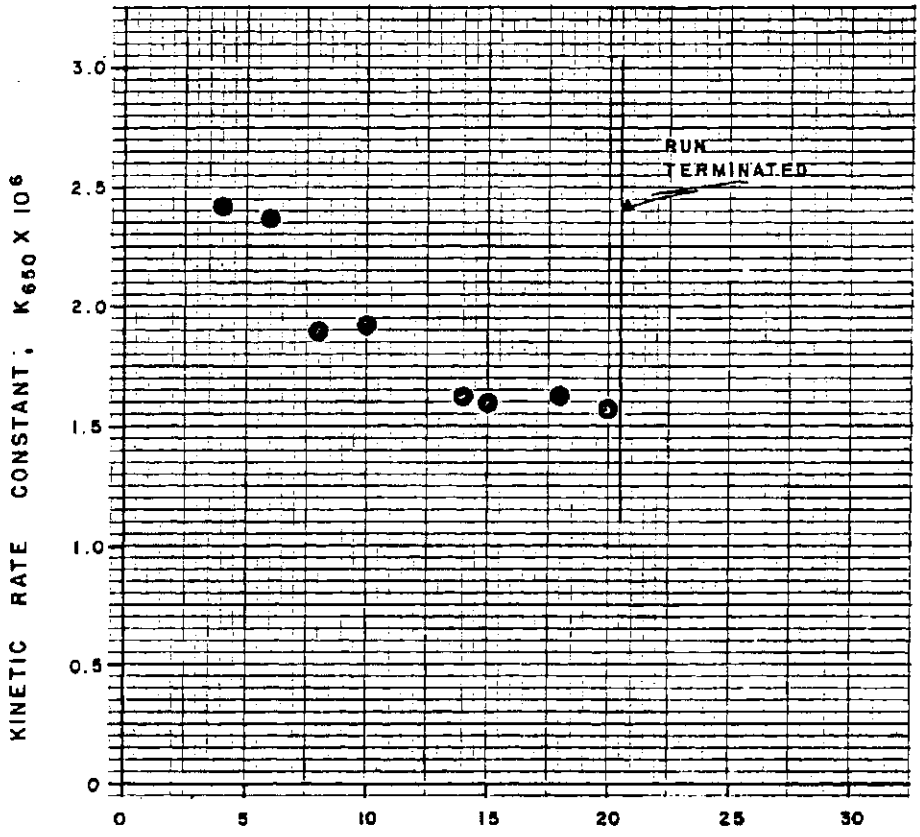
PROJECT NO. 664 DATE

FIGURE IV-C-13

CATALYST ACTIVITY VS. REACTION TIME

L P M P D U RUN # 15

GRACE CRG - A EXTRUDATES / FREEZENE - 100



CHEM SYSTEMS INC.
PROJECT NO. 6 6 4 DATE

was not considered a viable candidate for commercial operation and testing at the pilot plant.

6. Further Support Studies with Calsicat Catalyst

During March, 1978, the PDU operated with Calsicat Ni-230 S catalyst obtained from the LPM Pilot Plant. The objective of this run was to find out whether the catalyst had deteriorated because of long-term outdoor storage at IGT (this was suspected owing to its inferior performance in pilot plant Run #5).

The catalyst was reduced for 24 hours at 800°F. The test design bubble cap for introduction of gas and oil into the reactor was used. Reactivity values were based upon the compressor orifice flow values.

The first attempt at Run #16 was aborted shortly after start-up because solids had built up on the orifice plate. This buildup resulted in an oil flow reading much higher than the actual flow. The net effect was that the reactor was not properly fluidized, resulting in a hot spot temperature of 750°F and subsequent breakup and loss of catalyst. The next start-up successfully achieved approximately 28 hours of accumulated reaction time and 20 more hours of liquid only fluidization. Major events of PDU Run #16 are summarized in Table IV-C-22. A 40 percent loss in catalyst bed was observed over the first ten hours of reaction time (see Figure IV-C-14). When the reactor was emptied for examination, it was discovered that the bulk of this lost catalyst had settled below the bubble cap. To allow for a weld bead on the reactor body, the diameter of the bubble cap support plate had been reduced, creating a gap that let catalyst particles smaller than 5/64" pass into the cavity.

TABLE IV-C-22

SUMMARY OF EVENTS

PDU RUN # 16

DATE	TOTAL HOURS	REACTION TIME	EVENT
3/06/78	0	0	Reactor loaded with 11.0 lbs. Calsicat Ni-230S 3/32" Ø spheres obtained from the Pilot Plant. Heated under N_2 purge to 400°F.
3/07/78	18	0	Reactor switched to reduction gas (1.5% CO in H_2) and heated at a rate of 100°F/hr to 800°F.
3/08/78	40	0	Reactor switched to N_2, and temperature lowered to 650°F. Reactor then pressurized to 600 psig and isolated. System pressurized to 100 psig in order to initiate oil flow. System heated to 650°F and pressurized to 500 psig.
3/08/78	46	0	System at process conditions (650°F, 500 psig). Start feed gas to reactor at ~750 SCFH. Wet settled bed height is 85 cm.
3/08/78	47	1	Data point taken. Filter ΔP = 8.75.
3/08/78	48	2	Data point taken. Filter ΔP = 13.5.
3/08/78	49	3	Data point taken. Filter ΔP = 15.0. Bottom filter opened.
3/08/78	50.25	4.25	Data point taken. Filter ΔP = 2.8.
3/08/78	52.25	6.25	Data point taken. Filter ΔP = 8.4.
3/08/78	53/25	7.25	Data point taken. Filter ΔP = 8.4. Bottom filter apparently bypassing internally. Gas flow stopped. Oil flow to reactor switched to bypass.
3/08/78	55.25	7.25	Filters changed. Settled bed height = 60 cm. Restart oil and gas flow through reactor. Filter ΔP = 1.6.
3/09/78	56.25	8.25	Data point taken. Filter ΔP = 3.2.
3/09.78	57.25	9.25	Data point taken. Filter ΔP = 7.8.
3/09/78	58.25	10.25	Data point taken. Filter $\Delta P > 15.0$. Gas flow stopped. Oil flow to reactor switched to bypass.

TABLE IV-C-22 (continued)

SUMMARY OF EVENTS

PDU RUN #16

DATE	TOTAL HOURS	REACTION TIME	EVENT
3/09/78	61.0	10.25	Filter changed. Settled bed height = 50 cm. Restart oil and gas flow through reactor. Filter ΔP = 1.8.
3/09/78	62.0	11.25	Data point taken. Filter ΔP = 2.2.
3/09/78	63.0	12.25	Data point taken. Filter ΔP = 3.0.
3/09/78	64.0	13.25	Data point taken. Filter ΔP = 3.4. Leaking tube fitting results in fire. Reactor feed gas shut down. Reactor bypassed. Unit cooled down and depressurized with reactor isolated. All leaks are repaired, and unit restarted.
3/09/78	70.0	13.25	System at process conditions (650°F, 500 psig). Start feed gas to reactor at ~460 SCFH. Settled bed height = 50 cm. Restart oil and gas into reactor.
3/09/78	71.0	14.25	Data point taken. Filter ΔP = 5.4.
3/09/78	72.0	15.25	Data point taken. Filter ΔP = 8.6.
3/09/78	73.0	16.25	Data point taken. Filter ΔP = 14.4.
3/09/78	74.0	17.25	Data point taken. Filter ΔP = 15.0.
3/09/78	75.0	18.25	Data point taken. Filter $\Delta P > 15.0$. Gas flow stopped. Oil flow to reactor switched to bypass.
3/09/78	80.0	18.25	Filters changed. Settled bed height = 49 cm. Restart oil and gas into reactor.
3/10/78	81.0	19.25	Data point taken. Filter ΔP = 2.8.
3/10/78	82.0	20.25	Data point taken. Filter ΔP = 4.4.
3/10/78	83.0	21.25	Data point taken. Filter ΔP = 5.1.
3/10/78	84.0	22.25	Data point taken. Filter ΔP = 7.6.
3/10/78	85.0	23.25	Data point taken. Filter ΔP = 11.2.
3/10/78	86.0	24.25	Data point taken. Filter $\Delta P > 15.0$. Gas flow stopped. Oil flow to reactor switched to

TABLE IV-C-22 (continued)

SUMMARY OF EVENTS

PDU RUN #16

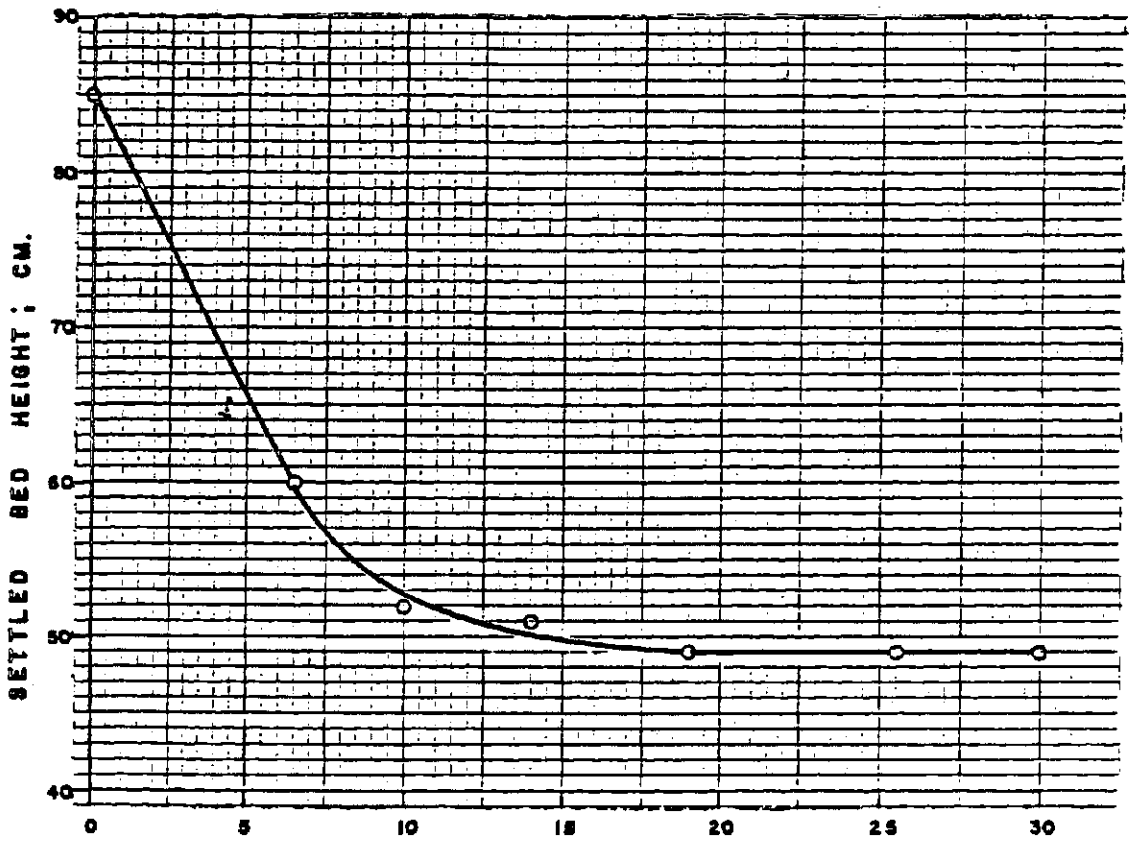
DATE	TOTAL HOURS	REACTION TIME	EVENT
			bypass.
3/10/78	88.25	24.25	Filter changed. Settled bed height = 49 cm. Restart oil and gas into reactor.
3/10/78	89.25	25.25	Data point taken. Filter ΔP = 1.8.
3/10/78	90.25	26.25	Data point taken. Filter ΔP = 2.3.
3/10/78	92.25	28.25	Data point taken. Filter ΔP = 3.6. Feed gas stopped. Liquid only through reactor.
3/10/78	102.25	28.25	Data point taken. Filter $\Delta P > 15.0$.
3/11/78	104.0	28.25	Filter changed. Settled bed height = 49 cm. Oil only flow.
3/11/78	112.0	28.25	Filter ΔP = 2.6. Data point taken. Run terminated. Settled bed height = 49 cm.

FIGURE IV-C-14

SETTLED BED HEIGHT VS. REACTION TIME

PDU RUN – 16

CALSICAT Ni – 230 S / FREEZENE – 100



Catalyst activity for Run #16, uncorrected for the aforementioned bed losses, was 1.0 X 10^{-6} gm-mol/(gm catalyst-atm-sec) (see Figure IV-C-15). The final activity level, corrected for bed loss, was 1.75 X 10^{-6} gm-mol/(gm catalyst-atm-sec). Catalyst attrition data for PDU Run #16 mirror pilot plant experience during Run #5. When the reactor was emptied at the end of the PDU run, visual examination of the catalyst showed particle breakage, confirming that the catalyst had been markedly weakened by changes in its physical characteristics brought about by long-term outdoor storage. Run #16 results are listed in Table IV-C-23.

7. Support Study with Catalyst Batch #038-A

In March, 1978, the PDU also operated with catalyst #038-A obtained from the batch to be tested in pilot plant Run #6. The objective of this run was to obtain laboratory-scale information for later comparison with pilot plant results.

The catalyst was reduced for 24 hours at a maximum temperature of 800^{0}F. Again, the test design bubble cap was utilized, and catalyst reactivities were calculated from compressor orifice flow values.

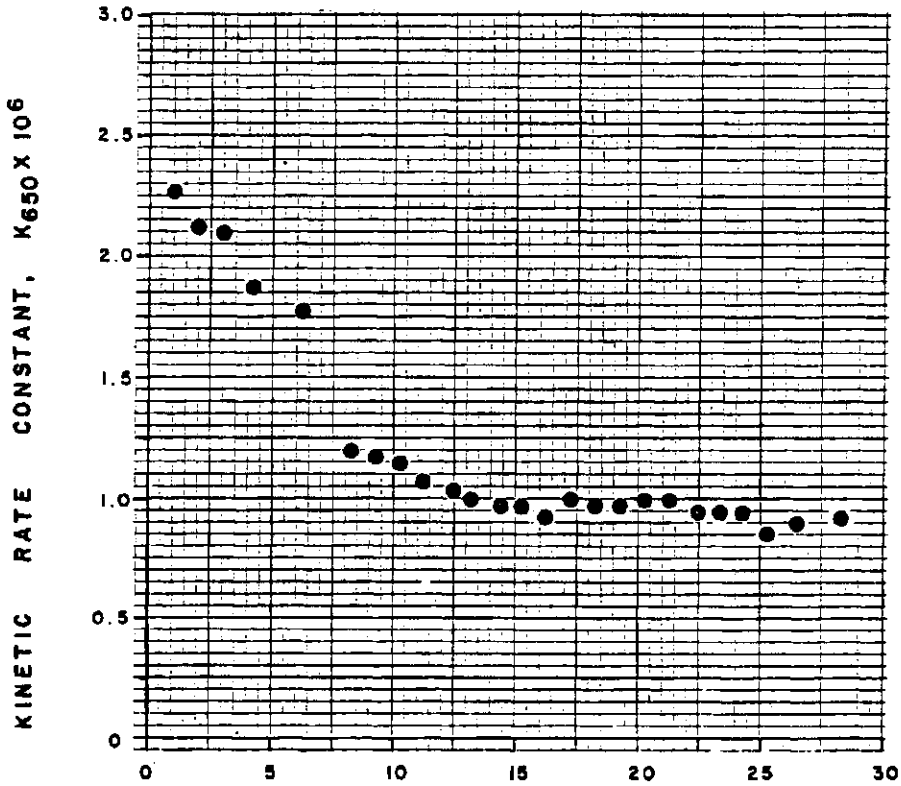
Approximately 13 hours of reaction time were accumulated in PDU Run #17 before massive, system-wide plugs forced termination of the run. The major events of this run are listed in Table IV-C-24. Catalyst activity had remained constant at 1.30 X 10^{-6} gm-mol/(gm catalyst-atm-sec) over the course of the run until the forced shutdown. PDU Run #17 results are summarized in Table IV-C-25. When the reactor was emptied, visual examination of the reactor contents revealed no discernible catalyst particles, only a granular, mudlike mass. Furthermore, catalyst fines had created a sludge that permeated the entire system, including the product separator.

FIGURE IV-C-15

CATALYST ACTIVITY VS. REACTION TIME

PDU RUN #16
CALSICAT Ni-230 S/FREEZENE-100

BASIS: 11.0 LBS. CATALYST



CHEM SYSTEMS INC.
PROJECT NO. 664 DATE

Table IV-C-23: LPM PDU Run #16 RESULTS

Accumulated Reaction Time (Hrs)	1	2	3	4.25	6.25	8.25
Feed Gas:						
H_2/CO Ratio	3.12	3.12	3.12	3.12	3.12	3.12
% H_2	75.75	75.75	75.75	75.75	75.75	75.75
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	24.25	24.25	24.25	24.25	24.25	24.25
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	4485	4485	4485	4550	4560	4545
Oil Flow Rate: GPM/Ft^2	90.2	90.2	90.2	90.2	90.2	90.2
Temperature (°F)	645	645	645	645	645	645
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	34.02	34.23	34.92	36.65	37.55	47.62
% N_2	—	—	—	—	—	—
% CH_4	58.09	57.71	56.38	53.97	52.56	36.80
% CO	3.85	4.00	4.67	5.52	6.11	11.28
% CO_2	4.04	4.05	4.03	3.85	3.77	4.29
% C_2^+	—	—	—	—	—	—
MW	12.86	12.86	12.83	12.64	12.56	11.42
SCFH	—	—	—	—	—	—
CO Conversion (%)	94.16	93.91	92.83	91.28	90.21	78.46
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	93.50	93.43	93.33	93.33	93.30	89.55
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	2.16	2.13	2.00	1.78	1.69	1.13
$K_{650°F}$ ($\times 10^6$)	2.27	2.13	2.10	1.87	1.79	1.19

Table IV-C-23: LPM PDU Run #16 RESULTS (continued)

Accumulated Reaction Time (Hrs)	9.25	10.25	11.25	12.25	13.25	14.25
Feed Gas:						
H_2/CO Ratio	3.12	3.12	3.12	3.12	3.12	3.12
% H_2	75.75	75.75	75.75	75.75	75.75	75.75
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	24.25	24.25	24.25	24.25	24.25	24.25
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	4550	4545	4535	4530	4525	2720
Oil Flow Rate:						
GPM/Ft^2	90.2	90.2	90.2	90.2	90.2	90.2
Temperature (°F)	645	645	645	645	645	645
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	48.28	48.45	50.15	50.52	51.74	42.15
% N_2	—	—	—	—	—	—
% CH_4	37.50	37.27	34.85	34.24	33.15	45.93
% CO	11.37	11.47	12.50	12.79	12.75	7.94
% CO_2	2.83	2.81	2.50	2.46	2.37	3.98
% C_2^+	—	—	—	—	—	—
MW	11.42	11.41	11.20	11.18	10.97	12.19
SCFH	—	—	—	—	—	—
CO Conversion (%)	77.99	77.74	74.93	74.16	73.59	86.27
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	92.99	93.00	93.30	93.29	93.34	92.02
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	1.11	1.09	1.02	0.99	0.97	0.92
$K_{650°F}$ (x 10^6)	1.17	1.15	1.07	1.04	1.02	0.97

Table IV-C-23: LPM PDU Run #16 RESULTS (continued)

Accumulated Reaction Time (Hrs)	15.25	16.25	17.25	18.25	19.25	20.25
Feed Gas:						
H_2/CO Ratio	3.12	3.12	3.12	3.12	3.12	3.12
% H_2	75.75	75.75	75.75	75.75	75.75	75.75
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	24.25	24.25	24.25	24.25	24.25	24.25
% CO_2	—					
% C_2^+	—					
VHSV (Hr^{-1})	2725	2720	2710	2715	2260	2255
Oil Flow Rate: GPM/Ft^2	90.2	90.2	90.2	90.2	90.2	90.2
Temperature (°F)	645	645	645	645	645	645
Pressure (psig)	500	500	500	500	500	500
Product Gas:						
% H_2	41.68	42.56	40.31	42.11	42.67	42.34
% N_2	—	—	—	—	—	—
% CH_4	46.66	45.35	48.40	46.01	44.90	45.59
% CO	7.80	8.20	7.56	7.94	8.38	8.05
% CO_2	3.88	3.88	3.73	3.94	4.05	4.02
% C_2^+	—	—	—	—	—	—
MW	12.21	12.14	12.33	12.19	12.19	12.19
SCFH	—	—	—	—	—	—
CO Conversion (%)	86.62	85.72	87.34	86.28	85.38	86.04
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	92.37	92.12	92.84	92.12	91.72	91.90
Catalyst Rate Constant:						
$K_{\bar{T}_R}$ ($\times 10^6$)	0.92	0.90	0.95	0.92	0.92	0.95
$K_{650°F}$ ($\times 10^6$)	0.97	0.94	1.00	0.97	0.97	1.00

Table IV-C-23: LPM PDU Run # 16 RESULTS

(continued)

Accumulated Reaction Time (Hrs)	21.25	22.25	23.25	24.25	25.25	26.25
Feed Gas:						
H_2/CO Ratio	3.12	3.12	3.12	3.12	3.12	3.12
% H_2	75.75	75.75	75.75	75.75	75.75	75.75
% N_2	—	—	—	—	—	—
% CH_4	—	—	—	—	—	—
% CO	24.25	24.25	24.25	24.25	24.25	24.25
% CO_2	—	—	—	—	—	—
% C_2^+	—	—	—	—	—	—
VHSV (Hr^{-1})	2265	2170	2265	2260	2500	2435
Oil Flow Rate: GPM/Ft^2	90.2	90.2	90.2	90.2	90.2	90.2
Temperature (°F)	645	645	645	645	645	645
Pressure (psig)	500	500	500	500	500	500
Product G						
% H_2	42.27	43.16	43.09	43.19	45.66	44.18
% N_2	—	—	—	—	—	—
% CH_4	45.72	44.22	44.26	44.32	40.61	42.90
% CO	7.92	8.51	8.59	8.60	10.09	9.35
% CO_2	4.08	4.11	4.06	3.89	3.64	3.57
% C_2^+	—	—	—	—	—	—
MW	12.20	12.16	12.16	12.10	11.86	11.96
SCFH	—	—	—	—	—	—
CO Conversion (%)	86.28	85.02	84.90	84.87	81.43	83.24
CO_2 Conversion (%)	—	—	—	—	—	—
CH_4 Selectivity (%)	91.80	91.49	91.59	91.92	91.78	92.31
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	0.95	0.91	0.91	0.91	0.80	0.85
$K_{650°F}$ ($\times 10^6$)	1.01	0.96	0.95	0.95	0.85	0.90

Table IV-C-23: LPM PDU Run #16 RESULTS
(continued)

Accumulated Reaction Time (Hrs)	28.25	28.25				
Feed Gas:						
H_2/CO Ratio	3.12	R				
% H_2	75.75	U				
% N_2	—	N				
% CH_4	—					
% CO	24.25	T				
% CO_2	—	E				
% C_2^+	—	R				
VHSV (Hr^{-1})	2435	M				
Oil Flow Rate:		I				
GPM/Ft^2	90.2	N				
Temperature (°F)	645	A				
Pressure (psig)	500	T				
Product Gas:		E				
% H_2	43.34	D				
% N_2	—					
% CH_4	43.34					
% CO	9.08					
% CO_2	3.74					
% C_2^+	—					
MW	12.03					
SCFH	—					
CO Conversion (%)	83.83					
CO_2 Conversion (%)	—					
CH_4 Selectivity (%)	92.06					
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	0.87					
$K_{650°F}$ (x 10^6)	0.92					

TABLE IV-C-24

SUMMARY OF EVENTS

PDU RUN #17

DATE	TOTAL HOURS	REACTION TIME	EVENT
3/27/78	0	0	Reactor loaded with 11 lbs of 1/8" Ø x 1/8" tablets of catalyst #0338-A obtained from the pilot plant. Heated to 400°F under N_2 purge.
3/29/78	24	0	Reactor switched to reduction gas (1.5% CO in H_2) and heated to 700°F for 5 hrs and then to 800°F overnight.
3/30/78	48	0	Reactor switched to N_2 and temperature lowered to 650°F while pressurizing to 550 psig and isolating. System pressurized to 200 psig and oil flow initiated. System heated to 650°F and 500 psig. Experienced incinerator start-up difficulty.
3/30/78	52	0	System at process conditions (500 psig, 650°F); initiated oil flow into reactor.
3/30/78	53.75	0	Initiated gas flow into reactor at~750 SCFH. Filter ΔP = 2.8 psi.
3/30/78	54.75	1	Filter $\Delta P > 15$ psi. Gas flow stopped. Oil flow to reactor switched to bypass.
3/30/78	56.50	1	Filter changed. Settled bed height = 77 cm. Restart oil and gas flow through reactor.
3/30/78	57	1	Data point taken. Filter ΔP = 8.0 psi.
3/30/78	58	2	Data point taken. Filter ΔP = 12.6 psi.
3/30/78	59	3	Data point taken. Filter ΔP 15 psi.
3/30/78	59.5	3.5	Gas flow stopped. Oil flow to reactor switched to bypass. Shutdown overnight. Settled bed height = 76 cm.
3/31/78	73.0	3.5	System heated to 650°F and pressurized to 500 psig.
3/31/78	75	3.5	System at process conditions (500 psig, 650°F). Initiated oil flow into reactor. Start feed gas flow at~980 SCFH.
3/31/78	76	4.5	Oil flow dropping. Feed gas shut off pending resolution of problems.

TABLE IV-C-24: (continued)

SUMMARY OF EVENTS

PDU RUN #17

DATE	TOTAL HOURS	REACTION TIME	EVENT
3/31/78	78.5	4.5	Restart oil and gas flow through reactor. Filter ΔP = 2.6 psi.
3/31/78	80	6	Data point taken. Filter P = 4.8 psi.
3/31/78	81	7	Data point taken. Filter P = 9.2 psi.
3/31/78	82	8	Data point taken. Filter P = 13.6 psi.
3/31/78	83	8.5	Data point taken. Filter P 15 psi. Gas flow stopped. Oil flow to reactor switched to bypass. Shut down over weekend. Filters changed.
4/03/78	144	8.5	System heated to 650°F and pressurized to 500 psig.
4/03/78	146	8.5	Initiated oil flow into reactor. Immediately plugged process oil filter. Oil flow to reactor switched to bypass. Filter changed. A 30 amp fuse on reactor salt bath is replaced; salt bath temperature drops to 450°F.
4/03/78	147.5	8.5	Oil flow switched to reactor.
4/03/78	148	8.5	Filter $\Delta P > 15$ psi. Switched oil flow to bypass reactor. Changed filters.
4/03/78	149	8.5	Filter $\Delta P > 15$ psi. Filter bypass opened; both filters isolated. Started gas feed.
4/03/78	162	9.5	Data point taken.
4/03/78	163	10.5	Data point taken.
4/03/78	164	11.5	Data point taken. Shut down overnight.
4/03/78	177	11.5	System heated to 650°F and pressurized to 500 psig.
4/03/78	178.5	11.5	Initiated oil flow into reactor. Experienced erratic oil flow rates. Fluidized bed height low. Started gas feed.
4/03/78	179.5	12.5	Pneumatic valves will not operate properly. Switched reactor to bypass flow. Unable to maintain minimum oil flow. Attempts to re-initiate oil flow unsuccessful. Massive plugging in system forced termination of run.

Table IV-C-25: LPM PDU Run #17 RESULTS

Accumulated Reaction Time (Hrs)	2	3	5.5	7	8.5	
Feed Gas:						
H_2/CO Ratio	2.88	2.88	2.88	2.88	2.88	
% H_2	74	74	74	74	74	
% N_2	—	—	—	—	—	
% CH_4	—	—	—	—	—	
% CO	26	26	26	26	26	
% CO_2	—	—	—	—	—	
% C_2^+	—	—	—	—	—	
VHSV (Hr^{-1})	4,888	4,888	4,813	4,813	4,813	
Oil Flow Rate: GPM/Ft^2	91	91	91	91	91	
Temperature (°F)	644	647	647	645	645	
Pressure (psig)	500	500	500	500	500	
Product Gas:						
% H_2	32.07	31.75	37.14	37.64	35.04	
% N_2	—	—	—	—	—	
% CH_4	53.23	53.53	45.52	45.37	46.98	
% CO	9.22	9.27	13.69	13.6	13.09	
% CO_2	5.48	5.46	3.37	3.4	4.89	
% C_2^+	—	—	—	—	—	
MW	14.18	14.22	13.38	13.34	14.06	
SCFH	—	—	—	—	—	
CO Conversion (%)	86.43	86.42	78.12	78.2	79.85	
CO_2 Conversion (%)	—	—	—	—	—	
CH_4 Selectivity (%)	90.66	90.75	83.11	93.03	90.57	
Catalyst Rate Constant:						
K_{T_R} ($\times 10^6$)	1.63	1.63	1.22	1.22	1.28	
$K_{650°F}$ ($\times 10^6$)	1.70	1.66	1.22	1.22	1.33	

Table IV-C-25: LPM PDU Run # 17 RESULTS
(continued)

Accumulated Reaction Time (Hrs)	10	11.5	12.5	12.5		
Feed Gas:						
H_2/CO Ratio	2.88	2.88	2.88	R		
% H_2	74	74	74	U		
% N_2	—	—	—	N		
% CH_4	—	—	—			
% CO	26	26	26	T		
% CO_2	—	—	—	E		
% C_2^+	—	—	—	R		
VHSV (Hr^{-1})	4,881	4,881	4,990	M		
Oil Flow Rate: GPM/Ft^2	91	91	91	I N		
Temperature (°F)	645	645	643	A		
Pressure (psig)	500	500	500	T		
Product Gas:				E		
% H_2	34.87	32.34	31.51	D		
% N_2	—	—	—			
% CH_4	50.66	52.70	51.88			
% CO	9.88	9.95	10.77			
% CO_2	4.59	5.01	5.85			
% C_2^+	—	—	—			
MW	13.62	14.09	14.55			
SCFH	—	—	—			
CO Conversion (%)	84.33	85.29	84.28			
CO_2 Conversion (%)	—	—	—			
CH_4 Selectivity (%)	91.69	91.32	89.87			
Catalyst Rate Constant:						
K_{T_R} (x 10^6)	1.52	1.56	1.51			
$K_{650°F}$ (x 10^6)	1.60	1.60	1.59			

Throughout the current series of PDU runs (#10 - #17), filters were on stream during combined oil and feed gas operations for about 3 - 5 hours before excessive pressure drop caused the oil to flow more slowly. When the main filter plugged, the feed gas was shut off and oil flow bypassed the reactor so the filter could be changed. At no time was the filter bypass valve opened.

The PDU did not operate in April, 1978. Upon completion of PDU Run #17, the unit was dismantled and cleaned. It was discovered that the H-101A heater elements had melted down and shorted to the heater shell, resulting in structural damage to the heater assembly. A new heater vessel and heater assembly were fabricated. In addition, a power supply and high temperature alarm were ordered. These replace a contactor and enable one controller to operate both H-101A and B heaters while surface thermocouples attached to the heater elements will be tied into an alarm system to prevent any excessively high temperatures.

Further modifications included relocating the old process oil filter and installing a second filter in an accessible locatian. This work necessitated relocating utilities and revamping the main process oil lines.

Modifications and repairs continued in May, 1978. A new heater vessel and heater element were delivered and installed. The heater power supply arrived on schedule late in May and was installed early in June. Relocation and installation of all utilities and process oil lines were completed. All differential pressure transmitters were cleaned, recalibrated, and reinstalled on their appropriate units. Modifications and repairs were completed in June including installation of the power supply, reinsulation of process piping and pressure testing of the unit. The PDU was then available for testing new or improved catalyst candidates for future use in the pilot plant or commercial size plants as necessary.