Section 6

LONG TERM ACTIVITY TESTS

One of the objectives of the experimental program was the demonstration of acceptable methanol synthesis catalyst activity levels over long periods of time (1-2 years). Initial experiments in the BSU had shown measurable drops in activity over the duration of only a several week period (calendar time). The unit was shut down and restarted each day. A series of experiments were run in the BSU, in which specific runs were repeated on a day-to-day basis in order to determine a typical activity-time pattern. Later on in the program, a series of continuous round-the-clock runs were performed using a Lurgi gas feed. The Bench Scale Unit was operated for 28 days. Three runs of six (6) days each were performed in a larger Process Development Unit (PDU). A second series of concurrent BSU and PDU runs were performed with a Koppers-Totzek type feed gas. These runs were of 30 days and 27 days duration in the BSU and PDU, respectively.

LURGI GAS

Bench Scale Unit Tests

Discontinuous Tests. The initial activity maintenance tests in the Bench Scale Unit examined the effect of temperature, pressure, and gas velocity (see Table 6-1 and Figure 6-1) using the Catalyst A (-16 +20 mesh)/Witco 40 mineral oil/Lurgi feed gas system. The BSU was operated 8 hours a day. When shut down over nights and intervening weekends, the reactor was in standby conditions. This consisted of maintaining the catalyst bed at temperature and pressure under no flow conditions. The base reaction conditions were 500 psig, 230°C with a 1,300 $Hr.^{-1}$ VHSV. These conditions were repeated daily for seven (7) days with no change in catalyst activity, yielding a CO conversion to methanol of about 28-30 percent. On the eighth day the reaction temperature was temporarily raised to 250°C to ascertain if this would cause any irreversible loss in catalyst activity. The base case point was then repeated for three more days, with still no apparent change in conversion. The feed gas rate was then raised in order to increase the actual gas velocity in the reactor to a value more typical of a commercial design case. This new

TABLE 6-1

DISCONTINUOUS CATALYST ACTIVITY MAINTENANCE
COMMERCIAL CATALYST A[1] (-16 +20 MESH)/
WITCO 40 MINERAL OIL/LURGI FEED GAS[2]

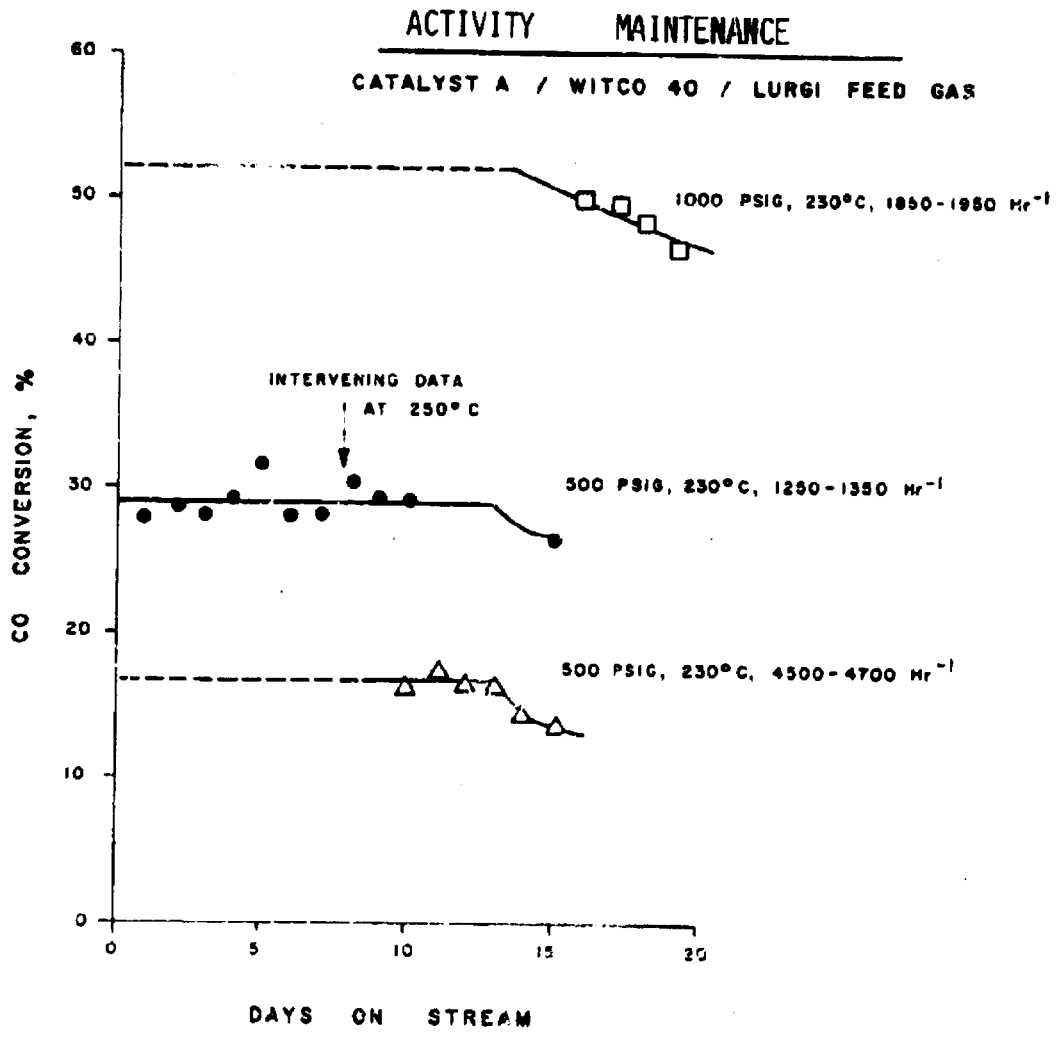
RUN NO.	TEMP. (°C)	PRESS. (psig)	VHSV Hr^{-1}	CO CONVERSION[3] (%)
75-1	230	500	1295	28.0
76-1	230	500	1275	28.8
77-1	230	500	1370	28.2
78-1	230	500	1315	29.6
79-1	230	500	1045	31.8
80-1	230	500	1245	28.0
81-1	230	500	1330	28.2
82-1	250	500	1345	20.7
82-2	230	500	1390	30.5
83-1	230	500	1365	29.1
84-1	230	500	4695	16.3
84-2	230	500	1300	29.3
85-1	230	500	4695	17.3
86-1	230	500	4575	16.2
87-1	230	500	4380	16.4
88-1	230	500	4570	14.4
89-1	230	500	4585	13.6
89-2	230	500	1046	26.3
90-1	230	1000	1870	50.5
91-1	230	1000	1870	49.8
92-1	230	1000	1895	43.6
93-1	230	1000	1865	46.7

(1) Catalyst loading = 219.6 gm = 180 cm^3.

(2) Nominal composition: 50% H_2, 25% CO, 10% CO_2, and 15% CH_4.

(3) Includes small selectivity to higher alcohols.

FIGURE 6-1


ACTIVITY MAINTENANCE
CATALYST A / WITCO 40 / LURGI FEED GAS
1000 PSIG, 250°C, 1850-1950 Hr⁻¹
INTERVENING DATA AT 250° C
500 PSIG, 250°C, 1250-1350 Hr⁻¹
500 PSIG, 230°C, 4500-4700 Hr⁻¹
CO CONVERSION, %
DAYS ON STREAM
0
10
20
30
40
50
60
0
5
10
15
20

condition was then repeated for a total of four (4) days. A constant activity level, measured by a CO conversion to methanol of 16-17 percent was achieved. However, on the following two days (days #15 and #16), there were successive, small drops in CO conversion, down to 14.4 percent and 13.6 percent respectively. The original conditions (VHSV = 1,300 Hr^{-1}) were repeated, and the results confirmed a small loss in catalyst activity. The CO conversion had dropped to 26.3 percent from its initial value of 28-30 percent. The effect of pressure on catalyst activity was tested by increasing the pressure to 1,000 psig, at 220°C with a 1,900 Hr^{-1} VHSV. The results for the four daily runs at these conditions showed small but noticeable losses in activity. Unfortunately, in attempting to repeat the original base conditions, an accidental rapid depressurization of the reactor forced discontinuance of this experimental program.

The loss in activity during the high pressure runs is unexplained. Contaminants in the feed gas supply were ruled out when subsequent experiments over a period of several weeks with this same gas supply resulted in an essentially constant level of activity. In addition, the spent catalyst did not show any unusual physical changes when it was removed from the reactor.

Continuous Tests. In January 1977, a one-month continuous run was completed in the Bench Scale Unit (see Table 6-2 and Figure 6-2). Catalyst A 3/32" Ø tablets, prepared by an outside vendor from the calcined Catalyst A powder, were used. The catalyst tablets contained 2 percent graphite (used as a pilling lubricant) and had a five pound average crush strength level.

After loading the reactor, the catalyst was reduced overnight with a premixed 2 percent H_2 in N_2 gas mixture and put on-stream using Witco 40 mineral oil as the circulating liquid. Except for a fifteen hour period, a Lurgi feed gas was used throughout the 650 hour test. Blending variations in the premixed gas resulted in lower H_2 (46-47 percent) and higher CO (26-27 percent) than the nominal 50 percent H_2 and 25 percent CO values normally associated with a Lurgi feed gas composition.

TABLE 6-2

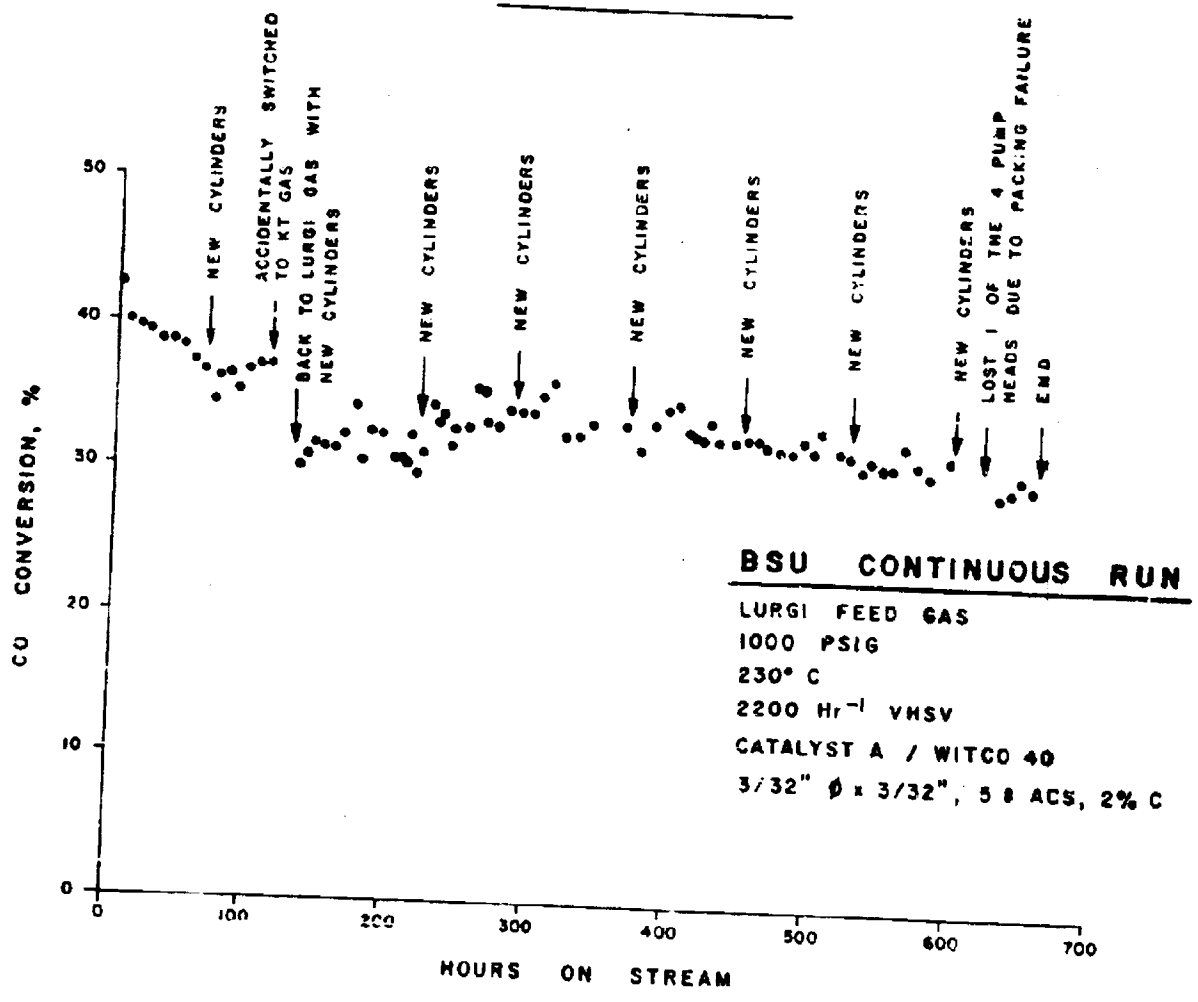
BENCH SCALE UNIT CONTINUOUS RUN

Catalyst A (3/32" Ø x 3/32" / Witco 40 Mineral Oil/Lurgi Feed Gas System

Nominal Operating Conditions: Temperature - 230° (±1%)
Pressure - 1000 psig (±2%)
Gas Feed Rate - 2200 liters Gas/Kg Cat-Hr (±5%)

HOURS ON STREAM	CO CONVERSION (%)	HOURS ON STREAM	CO CONVERSION (%)	HOURS ON STREAM	CO CONVERSION (%)
2	42.9	214	32.4	418	32.7
10	40.0	218	29.9	422	32.5
18	39.7	223	31.1	427	33.9
26	39.4	230	34.7	436	32.3
34	38.9	234	33.4	444	32.2
42	38.9	238	33.7	452	32.6
50	38.3	242	31.6	460	32.6
66	36.8	246	32.9	468	32.0
73	34.6	254	33.0	476	31.8
76	36.1	260	35.7	484	31.7
82	36.3	264	35.5	492	32.4
90	35.3	268	33.2	500	31.7
98	36.9	276	33.1	508	33.1
106	37.1	284	34.1	520	31.9
114	37.2	292	34.0	526	31.5
136	30.2	300	34.3	534	30.6
140	30.8	308	35.1	540	31.1
144	31.8	316	36.1	550	30.6
152	31.4	324	32.4	556	30.8
160	31.3	332	32.6	564	32.2
168	32.4	336	33.9	574	31.0
174	34.4	343	33.5	582	30.1
180	30.4	368	33.6	598	31.1
186	32.7	378	31.8	632	28.9
194	32.4	387	33.7	640	29.2
202	30.8	394	34.8	646	30.1
206	30.7	402	35.0	654	29.3
210	30.5	412	33.0		

FIGURE 6-2


CO CONVERSION, %
HOURS ON STREAM
0
10
20
30
40
50
0
100
200
300
400
500
600
700
NEW CYLINDERS
ACCIDENTALLY SWITCHED TO KT GAS
BACK TO LURGI GAS WITH NEW CYLINDERS
NEW CYLINDERS
NEW CYLINDERS
NEW CYLINDERS
NEW CYLINDERS
NEW CYLINDERS
NEW CYLINDERS
LOST 1 OF THE 4 PUMP HEADS DUE TO PACKING FAILURE
END
BSU CONTINUOUS RUN
LURGI FEED GAS
1000 PSIG
230° C
2200 Hr⁻¹ VHSV
CATALYST A / WITCO 40
3/32" Ø x 3/32", 5 8 ACS, 2% C

The initial activity level of 40-42 percent CO conversion was typical for this catalyst/liquid system at the operating conditions of 230°C, 1,000 psig and 2,200 Hr^{-1} VHSV. Over the first 90 hours, the conversion level slowly dropped to the 36-37 percent level, where it remained until the 115th hour. At that time, while attempting to switch to a new feed gas cylinder bank, inadvertently a KT type feed gas (38 percent H_2, 60 percent CO, and 2 percent CO_2) was used instead. This lasted for a period of 15 hours. When the system was returned to a Lurgi feed gas at the 130th hour, the CO conversion level had fallen 5 percentage points, down to the 30-32 percent level. The reason for this incremental loss in activity is unknown. Over the next 250 hours on-stream, the conversion level slowly rose 2 percent, an increase that cannot be solely explained by variations in different cylinder bank gas compositions. This recovery might be some indication of a (partial) recovery of the (temporary) deactivation due to the KT feed gas. Between the 400 hour and 600 hour points, the conversion slowly declined again, to the 30-32 percent level. At the 600th hour, one of the four pump heads of the circulating oil pump suffered a complete packing failure, which resulted in a rapid system depressurization, to 650 psig, before the head could be idled and isolated. After correcting the system upset, the system was again equilibrated, using only three-fourths of the original liquid flow, at the 29-30 percent conversion level. The run was terminated at the 655 hour mark. After cooling and depressurizing the system, the catalyst was removed from the reactor for physical and chemical analysis (see Section 4). Volumetric catalyst recovery was essentially complete, with no evidence of physical damage to the particles.

Process Development Unit Tests

Description of the Process Development Unit. The PDU was designed and constructed under ERDA Contract No. 14-32-0001- 1505, during the second phase of the Liquid Phase Methanation Process. The unit was used for methanol synthesis reaction without any modification. The detailed engineering design for the PDU is available in ERDA Report FE-1505-2, Liquid Phase Methanation, R and D Report No. 78.

The nominal feed gas rate for the unit is 1500 SCFH, which is a scale-up of 50-100 times the BSU. The PDU reactor is 3.62" I.D. x 7' high, and the catalyst bed height can be varied from 2 to 5 feet. The premixed synthesis gas feed is delivered to the laboratory in a tube trailer. A feed compressor is used to feed the gas into the reactor. In this manner, the pressure in the tube trailer can be reduced to 100 psig before a new supply is required. Two compressors are provided to allow flexibility in gas feed rate. The basic design and flow scheme of the PDU is similar to the bench scale unit. Product methanol and lesser amounts of vaporized oil are condensed out of the product gas stream. Phase separation occurs at ambient temperature, with a typical residence time in the product separator of one (1) hour. The oil is recycled back to the process oil circulating loop. The product gases, following analysis, are sent to an incinerator where they are thermally oxidized to carbon dioxide and water prior to discharge to the atmosphere. Sufficient instrumentation is provided for complete automatic control and monitoring from a remote control room. The system is designed for pressures up to 1000 psig and temperatures up to 750°F, and has operated satisfactorily at these conditions.

All the necessary gas streams are connected to a common manifold and are constantly purged to reduce sampling time lags. The selected gas stream may be directed to each column, in turn, to analyze for all the components of interest.

Discontinuous Tests. The original intent for the Process Development Unit program was to demonstrate scale-up for the liquid phase method and to perform process variable scans as done in the Bench Scale Unit. However, after deliberation with EPRI, it was decided that it would be far more valuable to conduct a shorter, one week continuous run, duplicating the conditions of the one month continuous BSU test. This would compare the effect of scale-up in a direct manner.

A short process variable scan was conducted in December 1976 to check out recent modifications made to the PDU. The reactor was loaded with 5 kilograms of the 3/32" Ø Catalyst A tablets (2 percent graphite, 5 pound

average crush strength) and reduced over a four-day period. A Lurgi feed gas was used for all the runs.

The results are presented in Table 6-3. On the first day the effect of feed gas flow at both the 500 and 1,000 psig level was investigated. The conversion levels were somewhat lower than obtained in the BSU for the same system and conditions. For example, Run 1-3 had a CO conversion level of 37.6 percent, whereas in recent BSU tests the conversion levels were almost 42 percent. On the second day when the conditions of Run 1-3 were repeated, the conversion dropped to about 35 percent (relative) of the original conversion level. All other runs performed on the second and third days of operation were internally consistent, with no further evidence of deactivation. The system response to all the process variables was predictable. The catalyst was removed from the reactor, with a sample sent to Dr. Kamil Klier of Lehigh University, for analysis, (see Section 4).

Continuous Tests. With the PDU mechanically operational, the reactor was reloaded with fresh 3/32" Ø Catalyst A tablets and reduced over a four day period. The system was put on-stream, to duplicate the continuous BSU test conditions; 230°C, 1000 psig and 200 hr^{-1} WHSV. The results are shown in Table 6-4 (Column A) and Figure 6-3. The initial conversion level of 35 percent was in line with the previously completed PDU variable scan. However, it was measurably lower than the initial 40-42 percent conversion level obtained in the concurrent continuous BSU test. More disturbing was the steep decline in CO conversion throughout the early hours of the test (four times faster than in the BSU). A decision was made to prematurely terminate the test and prepare for a second test run. One difference between the PDU and BSU tests was the reduction procedure used. In the PDU, reduction took nearly four days, compared to one day for the BSU catalyst charge. It was decided to duplicate the BSU test reduction procedures for the second PDU run. As can be seen in Column B of Table 6-4 and Figure 6-3, the one-day reduction procedure resulted in a moderate increase in conversion, up to the 38-39 percent level. However, it was again evident that the catalyst charge was under-going a fairly rapid decline in activity, at about 60 percent the rate of the first PDU test. There were several possibilities

TABLE 6-3

DISCONTINUOUS PROCESS DEVELOPMENT UNIT VARIABLE SCAN

Catalyst A[1] (3/32" Ø x 3/32", 2% C, 5 # ACS)
Witco 40 Mineral Oil
Lurgi Feed Gas[2]

PDU RUN NO.	TEMP. (°C)	PRESS. (psig)	FEED RATE (Std. Liters Gas/ Kg Cat-Hour)	CO CONVERSION (%)
1-1	230	500	1810	18.4
1-2	230	500	4225	9.6
1-3	230	1000	1710	37.6
1-4	230	1000	5070	16.8
2-1	230	1000	2030	24.7
2-2	270	1000	2015	24.9
2-3	250	1000	2080	25.6
2-4	250	500	2140	8.4
2-5	230	500	2165	8.1
3-1	230	500	2030	8.3
3-2	230	500	1150	12.1
3-3	250	500	1235	10.5
3-4	250	1000	2060	25.7
3-5	250	1000	1080	32.3

[1] Catalyst Loading = 5 Kg

[2] Actual Composition: 47.2% H_2, 26.1% CO, 12.2% CO_2, and 14.5% CH_4.

TABLE 6-4

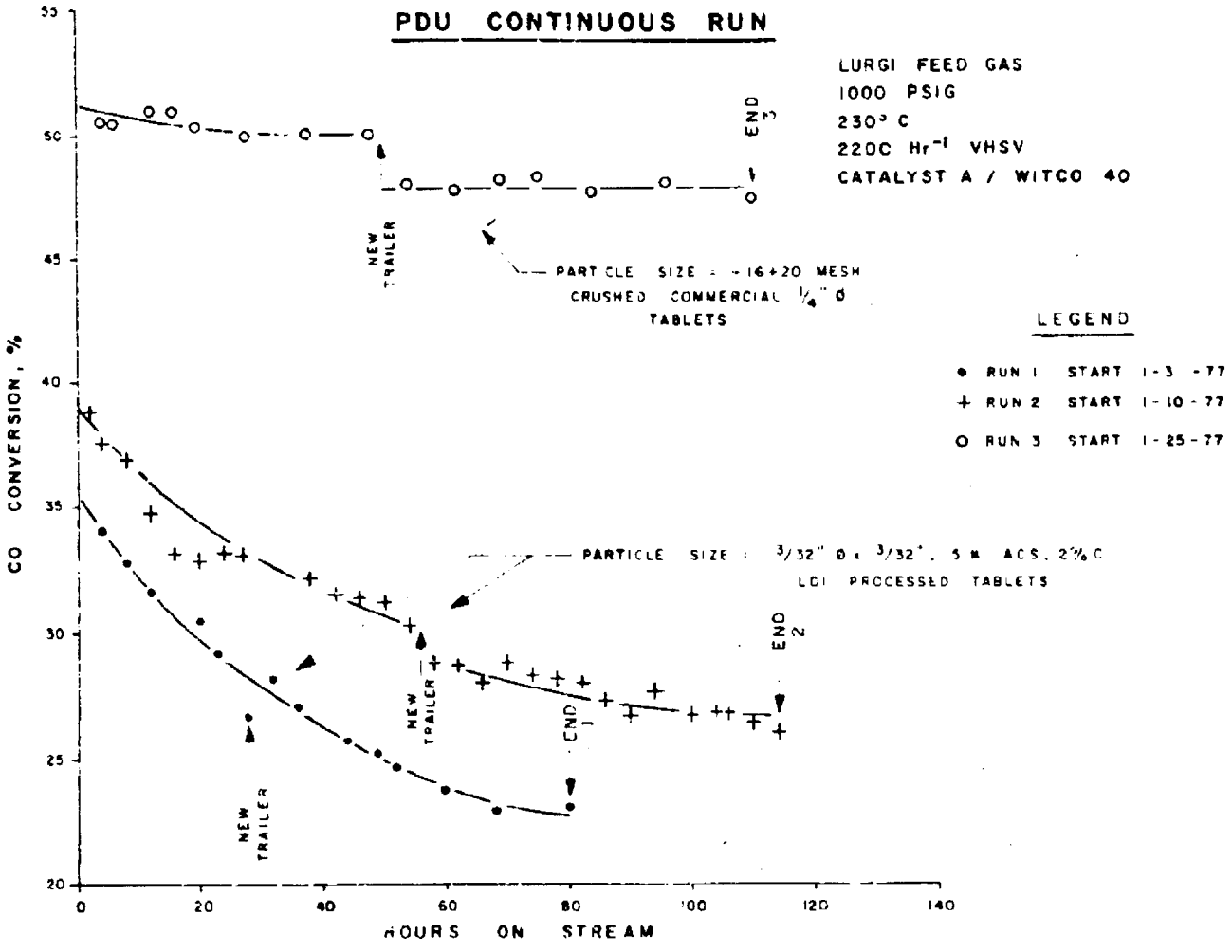
PROCESS DEVELOPMENT UNIT CONTINUOUS RUNS

Catalyst A/Witco 40 Mineral Oil/Lurgi Feed Gas System

Nominal Operating Conditions: Temperature - 230°C (±1%)
Pressure - 1000 psig (±1%)
Gas Feed Rate - 2200 Liters Gas/Kg Cat-Hr (±5%)
Liquid Role - 60 gpm/ft^2

(A) 3/32" Ø x 3/32"		(B) 3/32" Ø x 3/32"		(C) -16 +20 MESH	
HOURS ON STREAM	CO CONVERSION (%)	HOURS ON STREAM	CO CONVERSION (%)	HOURS ON STREAM	CO CONVERSION (%)
4	34.2	2	38.7	4	50.6
8	32.8	4	37.5	8	50.5
12	31.7	8	36.8	12	51.1
20	30.5	12	34.7	16	51.0
23	29.2	16	33.1	20	50.3
28	26.7	20	32.8	28	50.0
32	28.1	24	33.2	38	50.2
36	27.0	27	33.1	48	50.0
44	25.7	38	32.1	54	48.0
49	25.2	42	31.5	62	47.8
52	24.5	46	31.3	69	48.2
60	23.7	50	31.2	75	48.3
68	22.9	54	30.2	84	47.6
76	22.9	58	28.7	88	47.4
80	23.0	62	28.6	96	48.1
		66	27.9	110	47.9
		70	28.7		
		74	28.2		
		78	28.0		
		82	27.8		
		86	27.1		
		90	26.5		
		94	27.5		
		100	26.6		
		104	26.7		
		106	26.6		
		110	26.7		
		114	25.9		

FIGURE 6-3


PDU CONTINUOUS RUN
LURGI FEED GAS
1000 PSIG
230° C
220C Hr⁻¹ VHSV
CATALYST A / WITCO 40
END 3
NEW TRAILER
PARTICLE SIZE = -16+20 MESH CRUSHED COMMERCIAL 1/4" Ø TABLETS
LEGEND
RUN 1 START 1-3-77
RUN 2 START 1-10-77
RUN 3 START 1-25-77
PARTICLE SIZE = 3/32" Ø x 3/32", 5 M ACS, 2% C LCI PROCESSED TABLETS
END 2
END 1
NEW TRAILER
NEW TRAILER
CO CONVERSION, %
HOURS ON STREAM
55
50
45
40
35
30
25
20
0
20
40
60
80
100
120
140

that could cause this deactivation: (1) feed gas contamination, (2) process liquid contamination, (3) metals contamination due to other classes of catalyst previously used in the PDU unit, notably nickel methanation catalysts, and (4) catalyst preparation. Points (1) and (2) were eliminated when subsequent analysis of selected gas and process liquid samples showed non-detectable sulfur and chlorine levels, down to the 1 ppm level. In order to explore point (4) the catalyst preparation itself, commercially prepared 3/16" Ø tablets were hand crushed and sieved to provide a 5 kilogram catalyst charge in the -16 +20 mesh size range. This charge was reduced in one day, and a third PDU run initiated. The CO conversion rapidly equilibrated at the 50 percent level (see Column "C" in Table 6-4 and Figure 6-3). This is comparable to BSU runs with the same size catalyst. Except for a step change in conversion, down to the 48 percent level, when a different feed gas trailer use is used, the PDU operated stably for the balance of the run, an additional 60 hours. These results were highly encouraging in light of the first two runs.

Used catalyst from all three PDU runs, as well as from the BSU run were subjected to a substantial program of analysis at the Laboratory and at Lehigh University by Prof. Klier's group. The results of the inspections are presented in detail in Section 4 and summarized in Table 6-5.

The spent catalysts from the first two PDU runs had a high nickel content. Nickel could have originated from traces of methanation catalyst remaining in the PDU. There was no other contaminant or variable which directly correlates with the observed PDU performance.

Auger spectrographic analysis showed that remarkably the nickel concentration was not concentrated on the catalyst surface as one might expect for metals poisoning. The Auger determination is quantitatively sensitive down to about 1 percent concentration (compared to 0.15 percent in bulk catalyst), so a small concentration would not have been noticed.

TABLE 6-5

CATALYST INSPECTIONS FROM THE PDU PROGRAM
AND BENCH SCALE LIFE TEST

	SAMPLE DESCRIPTION	RUN DURATION (Days)	SURFACE AREA (M^2/g)	Fe (ppm)	Ni (ppm)
1.	Fresh Catalyst Tablets (3/32" x 3/32") Feed to first two PDU runs and bench scale run.	---	99	90	15
2.	Fresh 16 x 20 mesh Catalyst (ground and sized commercial tablets) Feed to third bench scale run.	---	88	90	15
3.	Spent catalyst from first PDU run.	4.5	83.7	186	1555
4.	Spent catalyst from second PDU run.	4.5	95.6	196	1275
5.	Spent catalyst from third PDU run.	4	90.6	143	289
6.	Spent catalyst from bench scale run.	28.0	85.7	414	52

KOPPERS-TOTZEK GAS

Continuous Bench Scale Unit and Process Development Unit Tests

Concurrent BSU and PDU round-the-clock continuous runs were performed during October-November, 1978, with a feed gas composition simulating a Koppers-Totzek coal gasifier effluent (after clean up)*.

Synopsis of BSU Run. The BSU run started on October 6, 1978 and was completed on November 5, 1978, after 720 hours on-stream. With the exception of a single two (2) hour period to replace a leaking sight glass, the unit operated at a temperature of 250°C, a pressure of 1000 psig, a KT gas feed rate of 3000 l/hr-kg catalyst, and a liquid rate of 60 gpm/ft^2.

Synopsis of PDU Run. The PDU run started on October 12, 1978 and was completed on November 10, 1978, after 645 hours on-stream. Operating conditions in the PDU were the same as in the BSU. During the run there were at least three occasions in which the PDU was placed in a standby condition. Two of the stoppages were due to a malfunction in the ZnO bed heater system, while the third was due to a loss of power. The hours accumulated under standby conditions are not included in the total on-stream time.

Carbon monoxide conversion versus the on-stream time is presented in Figures 6-4 for the BSU run and Figure 6-5, for the PDU run. Figure 6-5 also shows the PDU reactor fluidized bed height over the course of the run. The initial activity level in both units compared favorably; 16 percent CO conversion in the BSU, and 15 percent CO conversion in the PDU. Table 6-6 shows the alcohol product analyses from both units. These were quite similar to those obtained in previous runs with a KT gas. The PDU product had a slightly greater level of higher alcohols.

* Nominal composition: 34% H_2, 6% Ar, 58% CO and 2% CO_2

FIGURE 6-4

BSU CONTINUOUS RUN — KT GAS

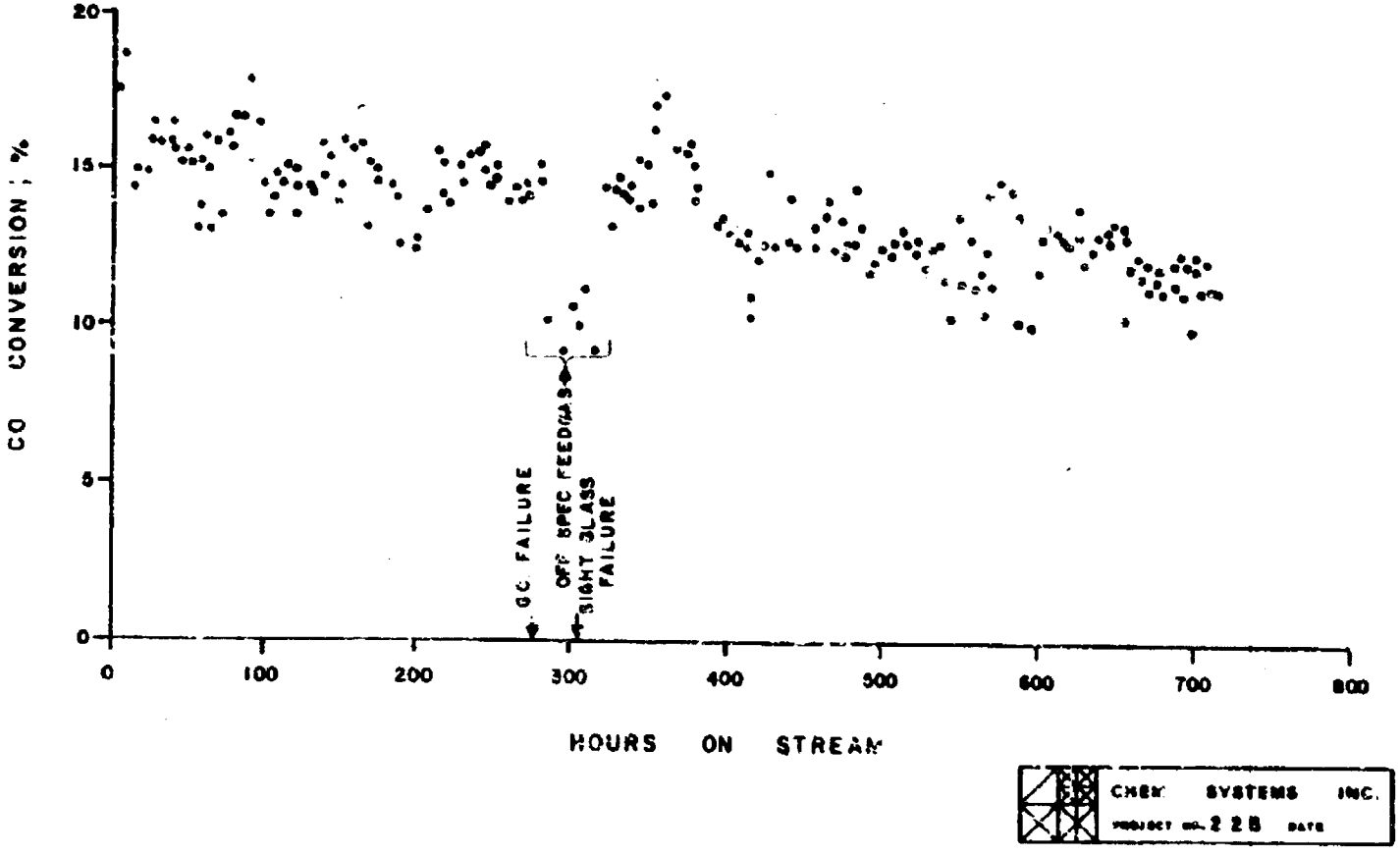


FIGURE 5-5

PDU CONTINUOUS RUN — KT GAS

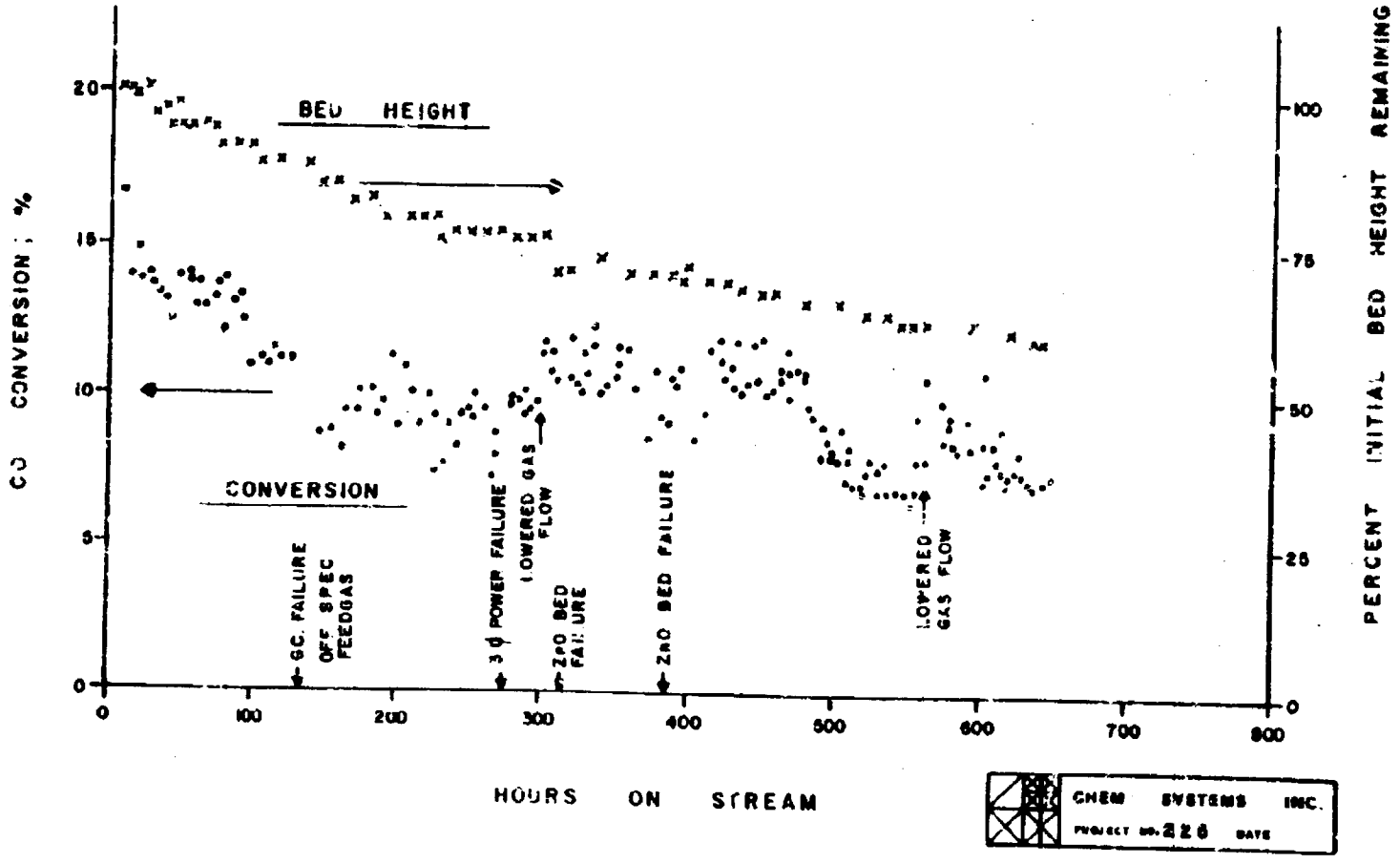


TABLE 6-6

30 DAY CONTINUOUS RUN(1): KT GAS/CATALYST A

	Product Alcohol Analysis-Oil Free Basis(2)	
	BSU	PXU
Methanol	93.0	91.8
Methyl Formate	0.4	0.3
Ethanol	2.1	1.1
i-Propanol	trace	trace
Methyl Acetate	0.4	0.2
n-Propanol	0.9	0.9
C_4 Alcohols	1.1	1.1
C_5 Alcohols	0.8	1.8
C_6 Alcohols	0.8	2.2
Water	0.5	0.6

(1) Nominal Conditions: 250°C, 1000 psig, 3000 liters gas/hr-Kg catalyst.

(2) See Figure 8-14 for typical oil level in product.

Throughout the BSU run there was a steady drift downward in CO conversion, to about 11.6 percent at the 720 hour mark. This decline in activity is not related to a loss in catalyst inventory, based on the weight and appearance of the recovered BSU catalyst. The BSU spent catalyst particles were regular in shape, retaining the sharp edged, cylindrical appearance of the dry oxide catalyst particle. The average particle dimensions and recovered weights from the BSU and PDU runs are presented in Tables 6-7 and 6-8, respectively. The slightly reduced dimensions for the recovered BSU catalyst, compared to the reduced oxide particles is most likely a result of the reduction procedure. While the standard deviation for the unreduced fresh catalyst and the BSU spent catalyst diameters are the same, the standard deviation for the length dimension is somewhat larger for the BSU spent catalyst. This is a result of a small number of particles fracturing across the diametrical plane. The recovered weight is slightly in excess of the loaded weight, which is due to residual process liquid remaining in the catalyst. This represents approximately 95 percent recovery since liquid saturated freshly reduced catalyst (219.6 grams) weighed 236.7 grams.

In sharp contrast to the physical appearance and recovered weight values for the BSU catalyst, the PDU catalyst particles showed gross dimensional changes, with a large number of particles appearing almost as spheres. The catalyst recovery from the PDU run was only 64.2 percent.* This agrees well with the relative average particle volumes for the recovered PDU and BSU catalysts. The ratio of PDU average particle volume to BSU average particle volume is 0.656**, which indicates that the primary mode of catalyst loss in the PDU run was through steady particle attrition. This is also confirmed by the fluidized catalyst bed height at the conclusion of the PDU run period (53 cm), at 60 percent of the initial height (90 cm).

* PDU Recovery $= 100 \times \frac{219.6}{236.7} \times \frac{3464}{5000} = 64.2\%$

** $\frac{\text{PDU Particle Volume}}{\text{BSU Particle Volume}} = \frac{4.37}{5.25} = 0.656$

TABLE 6-7

CATALYST WEIGHT RECOVERY - 30 DAY CONTINUOUS RUN

	BSU	PDU
Loaded as a Dry Oxide; gm	219.6	5,000(1)
Recovered as Oil Saturated and Reduced; gm	226.4(2)	3,464

(1) Settled bed height = 63 cm.

(2) Recovery for a standardizaton run of zero hour duration was 236.7 gm.

TABLE 6-8

AVERAGE CATALYST PARTICLE DIMENSIONS - 30 DAY CONTINUOUS RUN

	Fresh Oxide	Recovered from BSU	Recovered from PDU
Diameter; in x 10^3	92 ± 1	98 ± 1	79 ± 6
Length; in x 10^3	88 ± 1	86 ± 4	70 ± 7
Volume(1); $in^3 \times 10^4$	5.85	5.23	3.43

(1) Volume = $\frac{\pi}{4} \frac{\sum_{i=1}^{N} d_i^{2/1}}{N}$

During the course of the PDU run, the gas flow was reduced twice to compensate for the measured (by fluidized bed height) loss of catalyst. This was done at the 300 hour mark and at the 560 hour mark. This was done to maintain a constant gas space velocity in order to monitor the intrinsic catalyst activity. After both adjustments the CO conversion did increase but not up to a level equivalent to the BSU run. It appears from the data that the decrease in catalyst activity increased with run time. There appears to be a loss in contacting efficiency with loss in bed height, which further complicated the analysis of the data.

Oil degradation rates are negligible at these reaction conditions. However, oil make-up rates of 1-2 gallons per day were necessary to compensate for materials handling losses and leaks.

In addition to the physical property measurements, samples of the recovered BSU and PDU catalyst were analyzed for nickel and iron content as presented in Table 6-9. The nickel levels are intermediate to those found in the previous continuous runs. Iron content was surprisingly high. It was expected that the ZnO guard chambers should scavenge any iron present as iron carbonyl. The high iron content of the PDU spent catalyst may account for the larger amounts of higher alcohols in the PDU methanol product, as compared to the BSU methanol product.

The results of these runs are inconclusive, regarding catalyst life. Temperature programming can be used to compensate for slow activity decline, as done in other processes. Additional work is required in catalyst development in order to improve attrition resistance.

TABLE 6-9

TRACE METAL ANALYSIS - KT GAS 30 DAY CONTINUOUS RUNS

	BSU	POU
Nickel (1)	480	780
Iron (2)	600	1,660

(1) Fresh catalyst level - 15 ppm
(2) Fresh catalyst level - 90 ppm