

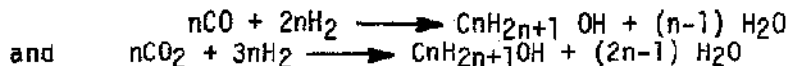
where  $X'_{CO}$  = Corrected carbon monoxide conversion to ALKANOL and light hydrocarbons;  
 $y_{CO}$  = Total carbon monoxide conversion as determined from the Carle gas chromatographic analysis;  
 $y_{CO/CO_2}$  = carbon monoxide conversion to carbon dioxide as determined from the Carle instrument.

a. Analysis of 292-Hour Campaign With Freshly Reduced Catalyst

During the 292-hour test, the performance of the catalyst was monitored in terms of activity as measured by both carbon monoxide conversion per pass and oxygenates space time yields and in terms of product selectivity (gas to ALKANOLS ratios as well as ALKANOLS composition). The Schulz-Flory distribution was also applied to the analysis of the data.

Some changes to the reaction conditions were made during the course of the test which may have affected the observed performance of the catalyst. These changes comprised varying the composition of the synthesis gas fed to the reactor. Although the bulk of the testing was with gas composition #1 shown in Table VI-7, some additional testing was carried out with synthesis gases having differing hydrogen/carbon monoxide ratios, carbon dioxide contents and balance ratios\*.

\*The balance ratio represents the stoichiometric synthesis gas requirement for total conversion of synthesis gas to alcohol product based on the equations:



It can be shown that the balance ratio,  $H_2/(CO + 1.5 CO_2)$ , should be 2.0 for 100% selectivity to alcohol products. Coproduction of hydrocarbons requires a higher balance ratio to reflect the stoichiometry of the hydrocarbon formation reactions. For paraffins, the balance ratio of  $H_2/(CO + 1.17 CO_2)$  should be 3.0. The balance ratio is used to characterize the "balance" of the reactants relative to stoichiometric requirements. Operation at the balance point will correspond to essentially total conversion of CO and CO<sub>2</sub> to the respective products whereas operation at low balance ratios will limit the degree of carbon oxides conversion. In practice, the actual balance ratios are about 5% higher in order to account for purge of inerts.

TABLE VI-7

SYNTHESIS GAS COMPOSITIONS STUDIED  
DURING FIRST 292-HOUR TEST CAMPAIGN WITH UCI L-1122  
CATALYST IN THE BERTY REACTOR

	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
<u>Volume Percent</u>						
Hydrogen	50.4	57.0	58.0	32.3	46.0	67.0
Argon	14.3	10.0	11.5	4.8	14.0	0
Carbon Monoxide	24.5	28.0	29.0	57.6	34.0	33.0
Carbon Dioxide	10.8	5.0	1.5	5.3	6.0	0
Molar Ratio of H <sub>2</sub> /CO	2.0	2.0	2.0	0.56	1.35	2.0
Stoichiometric Balance Ratio, [H <sub>2</sub> /(CO + 1.5 CO <sub>2</sub> )]	1.24	1.61	1.86	0.49	1.07	2.03

• Effect of Catalyst Aging

Over the 292 hour test period, the carbon monoxide conversion to ALKANOLS and hydrocarbon gas products was increasing with time as illustrated in Figure VI-1 at constant reactor temperature, pressure and space velocity. The carbon monoxide conversion at the 292-hour point was about 24 percent per pass or about 2.6 times that of an early test point taken at about 25 hours on-stream time. The catalyst productivity, as measured by space time yield to ALKANOLS, also increased with on-stream time (Figure VI-2) by a factor of about 1.5-2.0.

A catalyst activity increase with on-stream time is not a common phenomenon during synthesis gas conversion processes. In fact, a more common phenomenon is deactivation due to carbon deposition, sintering, etc. However, the ALKANOLS synthesis is extremely complex involving the production of a large spectrum of hydrogenated and oxygenated products. During the test, it was also observed that the conversion of carbon monoxide to certain products was decreasing with time (e.g., methanol) whereas the conversion to other products (e.g., C<sub>2</sub>-C<sub>6</sub> oxygenates) was increasing with time. The net result was that the rate of increase in the conversion to C<sub>2</sub>+ components of ALKANOLS exceeded the rate of decrease in the conversion to methanol (Figure VI-3).

This phenomenon is more clearly depicted in a series of graphs showing the change in ALKANOL product composition with on-stream time for all of the test points obtained under varying conditions of space velocity and synthesis gas composition. The relevant graphs are described as follows:

<u>Figure No. (VI- )</u>	<u>Title</u>
4	Methanol Content of ALKANOLS Vs. On-Stream Time For UCI L-1122 Catalyst
5	C <sub>2</sub> -C <sub>6</sub> Oxygenates Content of ALKANOLS Vs. On-Stream Time For UCI L-1122 Catalyst
6	C <sub>4</sub> -C <sub>9</sub> Hydrocarbon Content of ALKANOLS Vs. On-Stream Time For UCI L-1122 Catalyst

FIGURE VI-1

CORRECTED CO<sub>2</sub> CONVERSION VS. HOURS ON STREAM FOR  
 VC-1-1122 CATALYST IN BERRY REACTOR

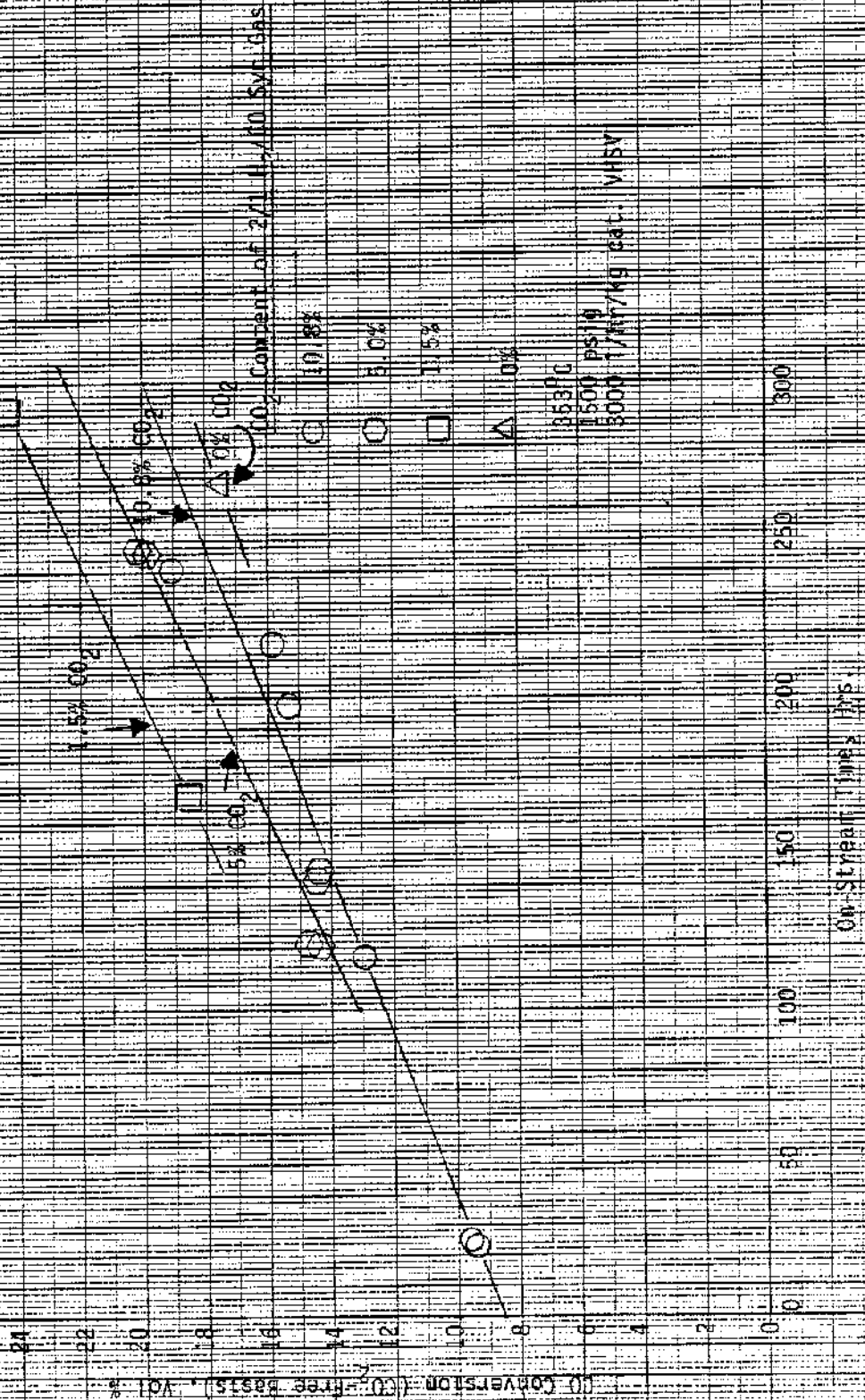


FIGURE VI-2

SPACE TIME YIELD TO ALKANOLS VS. ON-STREAM

TIME FOR UBIT L-1122 CATALYST

CO<sub>2</sub> Content of Syn Gas

Space Time Yield to Alkanols, gmoL C/hr/Kgm Catalyst

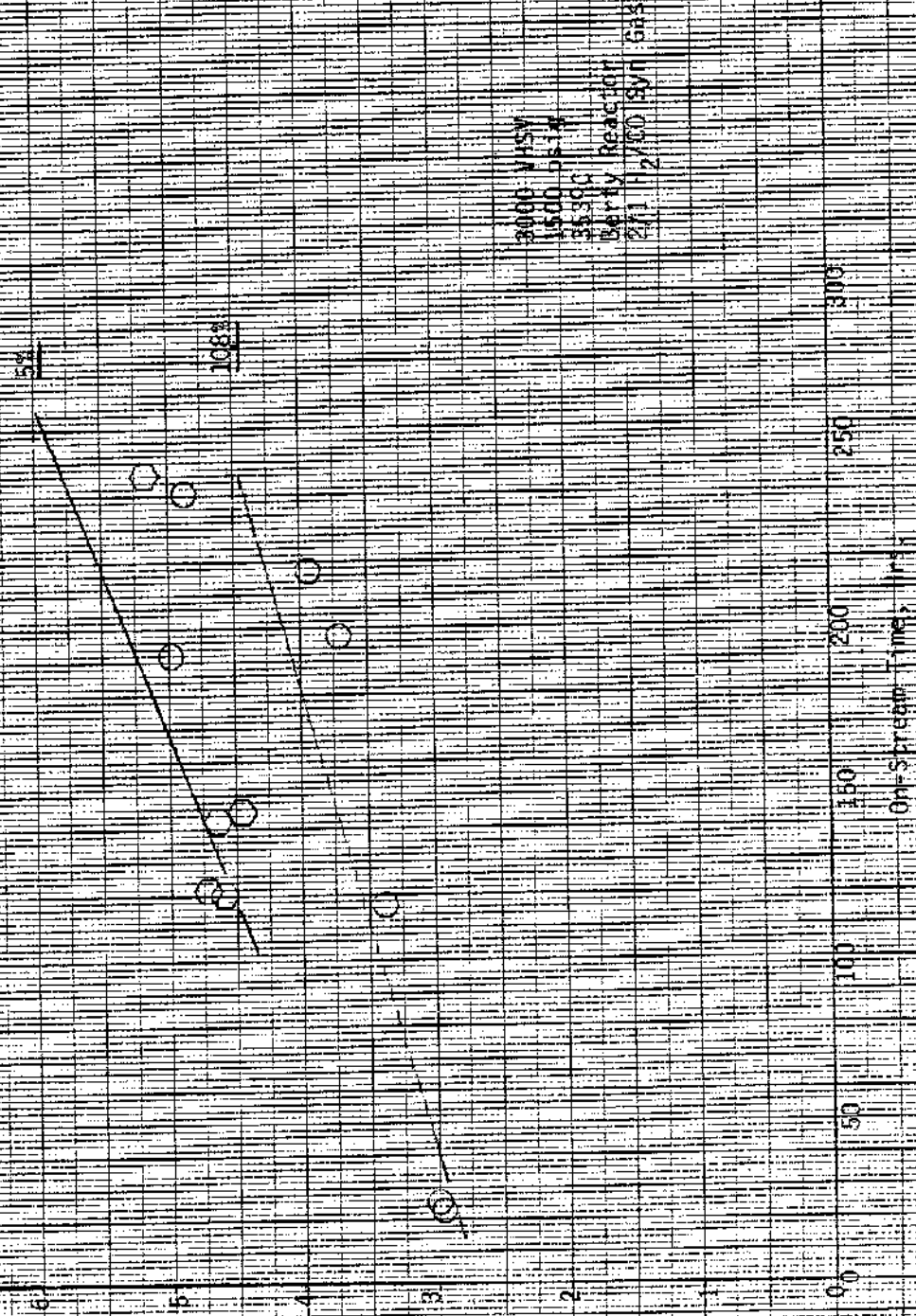


FIGURE VI-3

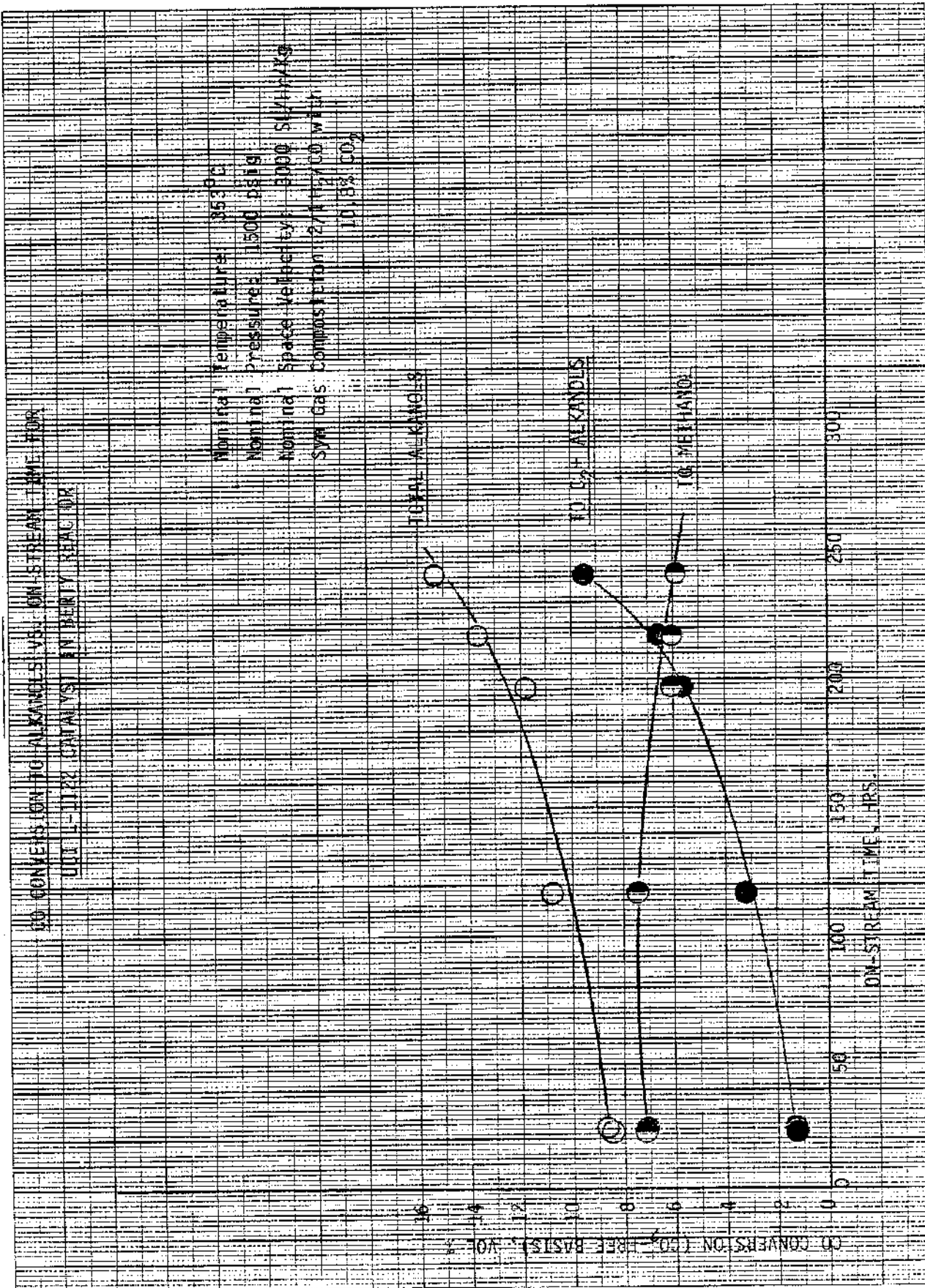


FIGURE VI-4  
METHANOL CONTENT OF ALKANOL MIXTURES  
ON-STREAM TIME FOR UCI LIBZ CATALYST

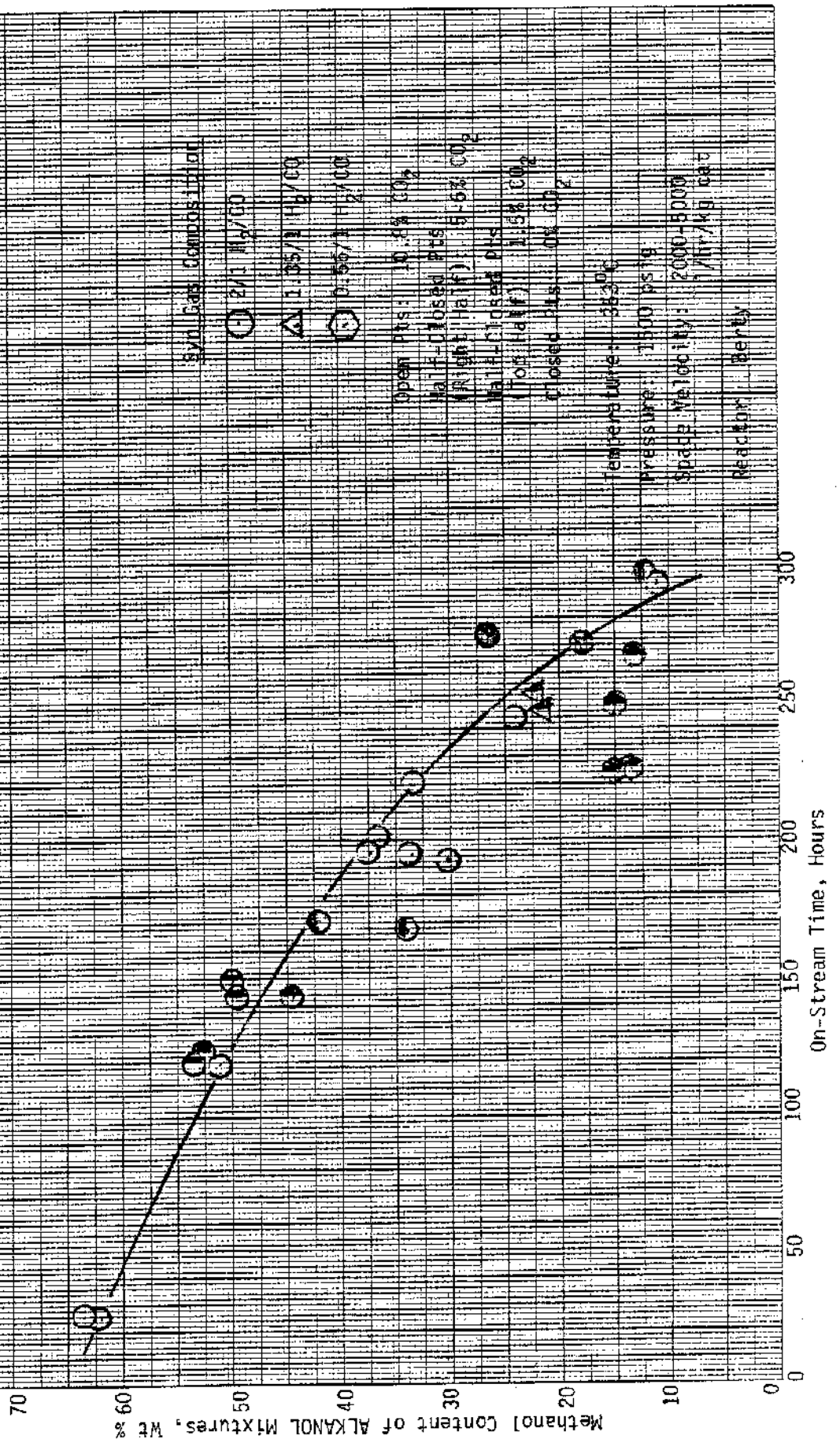




FIGURE VI-5

C<sub>2</sub>-C<sub>6</sub> OXYGENATES CONTENT OF ALKANOLS  
 VS. ON-STREAM TIME FOR UC L-1122 CATALYST

Syn Gas Composition

○ 2/1 H<sub>2</sub>/CO

△ 1.35/1 H<sub>2</sub>/CO

○ 0.8/1 H<sub>2</sub>/CO

Open Pts: 10.8% CO<sub>2</sub>

Half-Closed  
 (Right Half): 5-6% CO<sub>2</sub>

Half-Closed  
 (Bottom Half): 1.5% CO<sub>2</sub>

Closed Pts: 0% CO<sub>2</sub>

Temperature: 353°C

Pressure: 1100 psig

Space Velocity: 2000-5000  
 l/hr/kg cat

Reactors: Berty

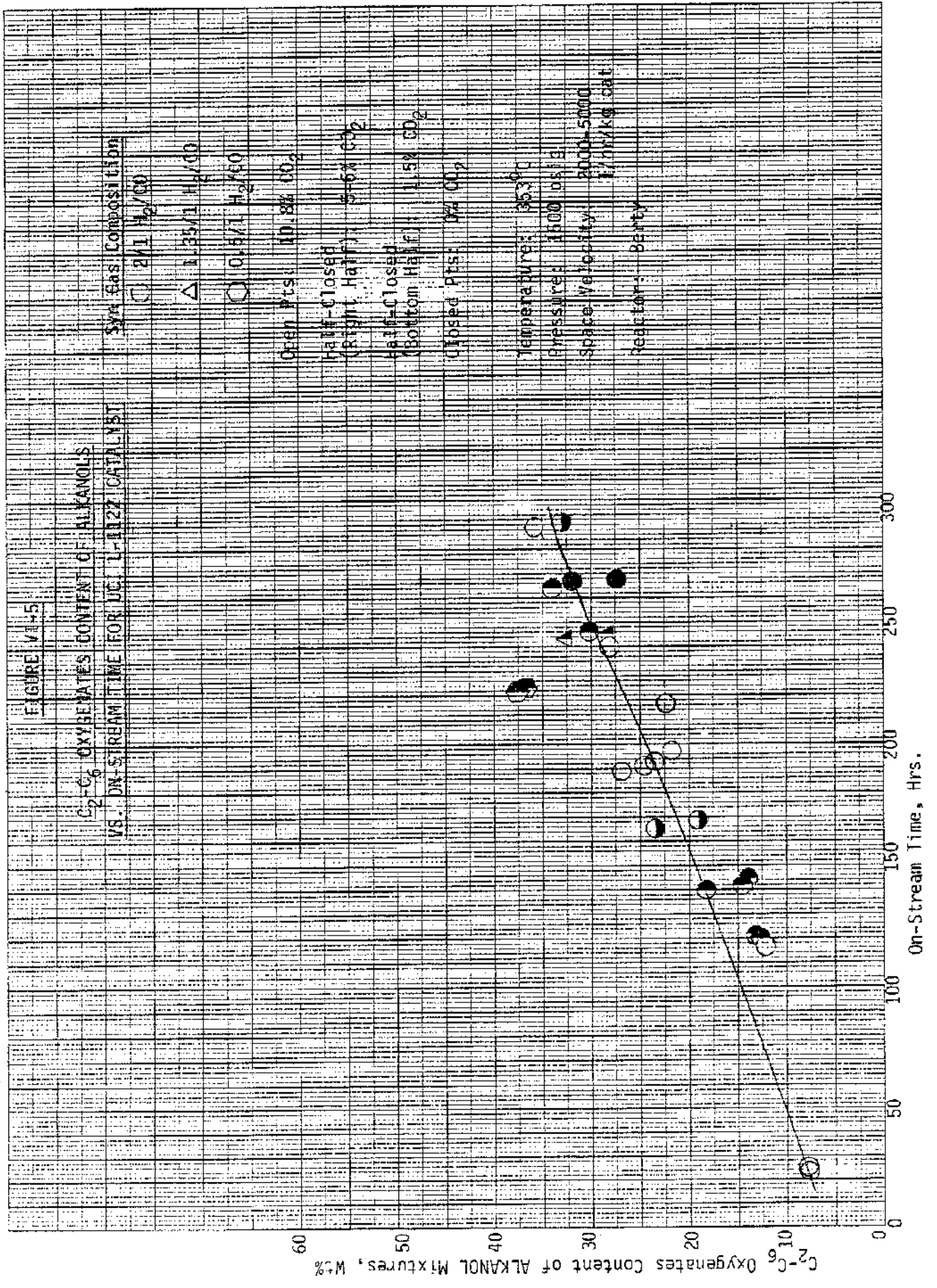
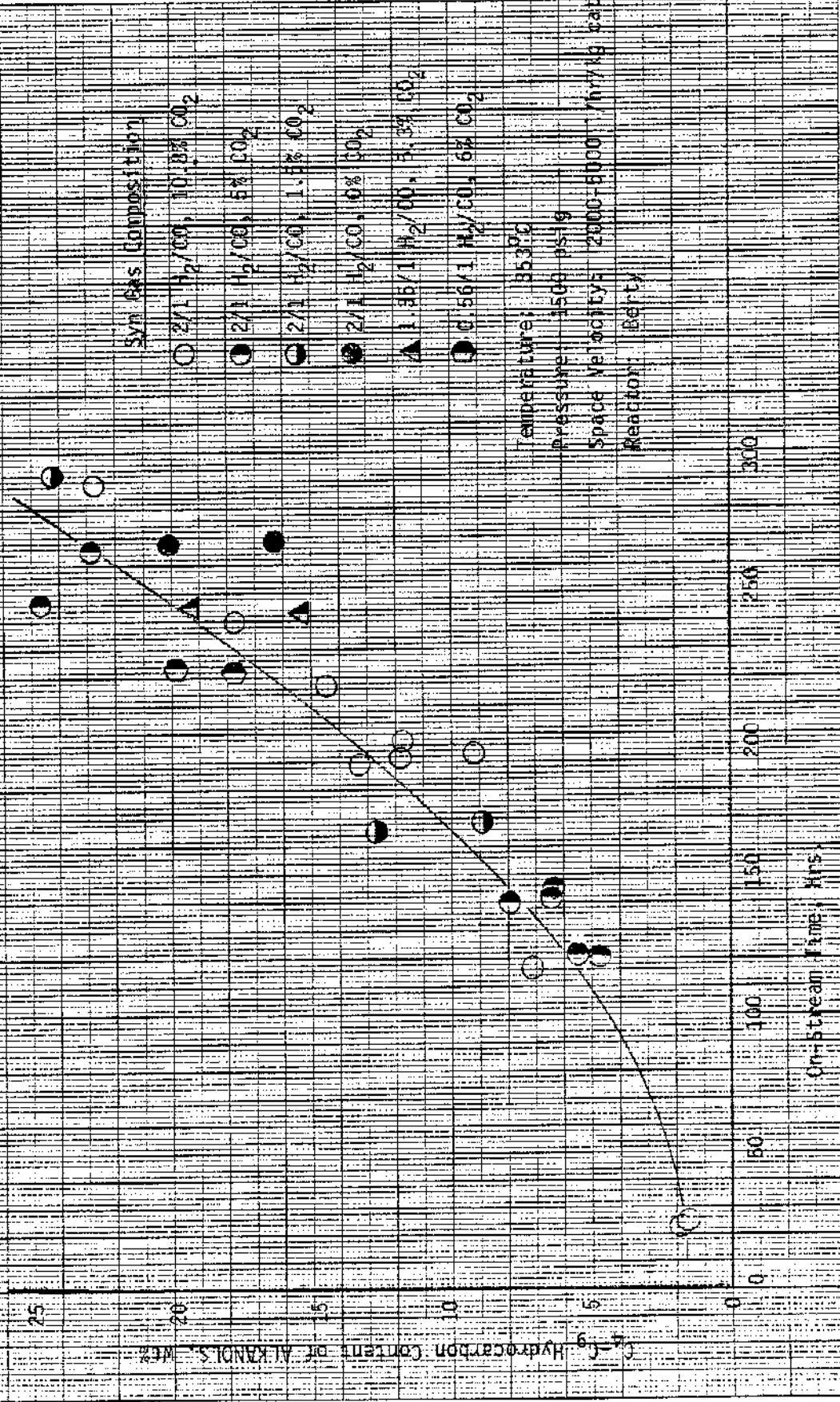




FIGURE VII-6

C<sub>4</sub>-C<sub>9</sub> HYDROCARBON CONTENT OF ALKANOLS VS. ON-S-REAN TIME FOR UCI-1, 1122 CATALYST

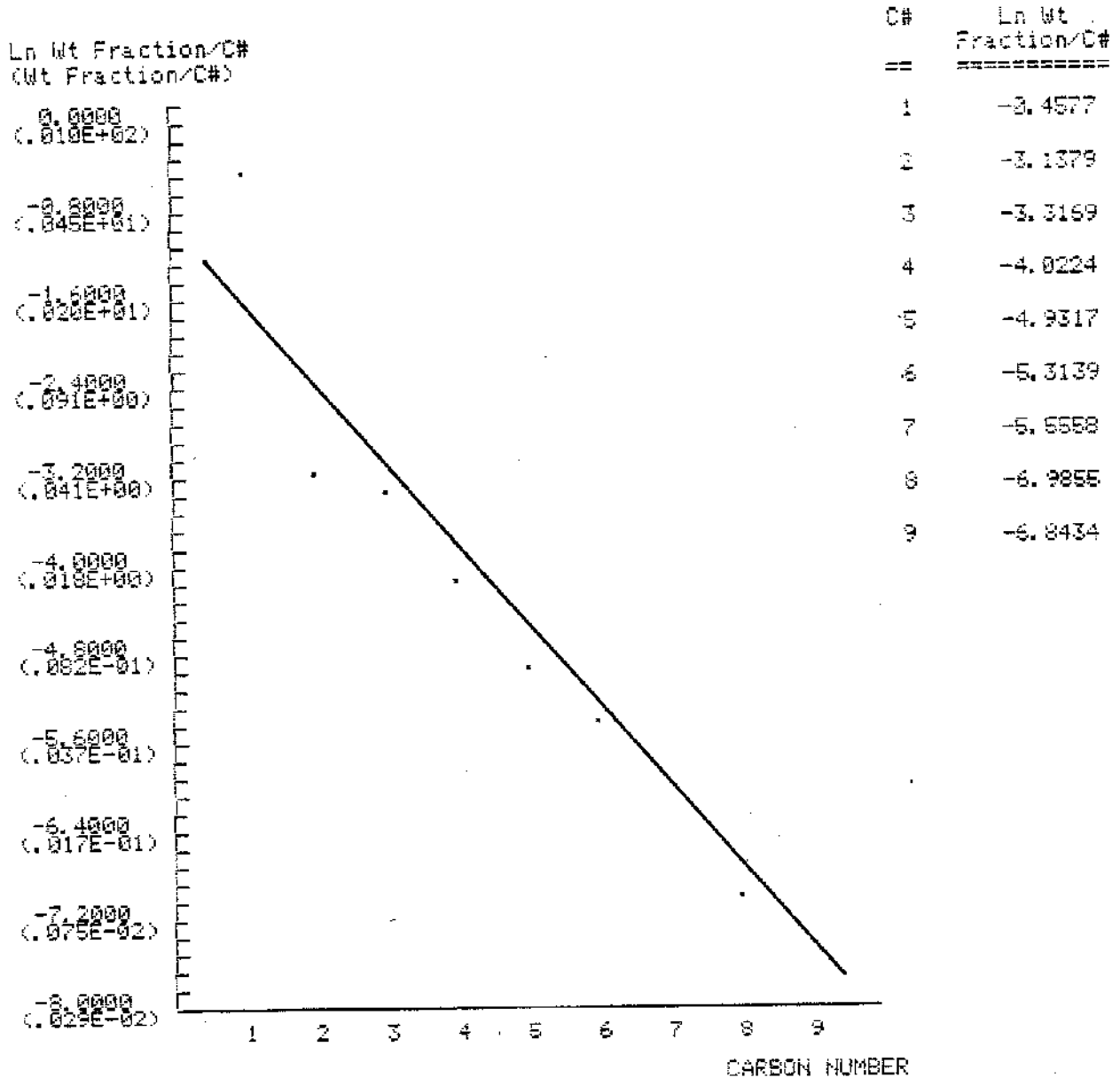


From the figures, it can be seen that the methanol content decreased almost linearly over the 292-hour test period to a value of about 42 weight percent from its early value at 20 hours on-stream time of about 92 weight percent. This 50 percent decrease in methanol content corresponded to an almost equivalent increase in the  $C_2+$  content of the ALKANOL mixture with the  $C_2-C_6$  oxygenates/ $C_4-C_9$  hydrocarbons ratio of about 6/5. This suggests that a polymerization mechanism might have been controlling during the catalyst compositional changes occurring over the 292-hour test duration. A typical modified Schulz-Flory distribution plot for L-1122 catalyst tested in the Bertly reactor is shown in Figure VI-7. When these data were analyzed by use of the modified Schulz-Flory distribution relationship, it was determined that the degree of polymerization was increasing with on-stream time. This finding has been plotted in Figure VI-8 which shows the modified Schulz-Flory probability parameter increasing linearly with on-stream time from about 0.2 to 0.6 over the first 250 hours on-stream time and then lining out at a value of 0.6. The value of the modified Schulz-Flory probability parameter just after the catalyst is placed on-stream should be indicative of the characteristics of the freshly reduced and unaged L-1122 catalyst. A linear extrapolation of the data in Figure VI-8 to zero on-stream time suggests that the initial modified Schulz-Flory probability parameter for this catalyst was 0.20. A value of 0.20 indicates that no more than about 3 percent of the synthesis products will have a carbon number in excess of three. This compares to a maximum of about 48 percent concentration for synthesis products having carbon numbers in excess of three for the case of a modified Schulz-Flory probability of 0.60 (observed at 292 hours on-stream time). For comparison purposes, a typical Fischer-Tropsch catalyst has a Schulz-Flory probability parameter of 0.80 which indicates that the concentration of synthesis products having carbon numbers in excess of three is about 82 percent. Again, it should be noted that the modified Schulz-Flory distribution equation utilized to analyze ALKANOLS synthesis products does not make any distinction between the class of compound, i.e., alcohol, paraffin or olefin, for any given carbon number. However, for the bulk of the test data, the alcohol products predominated in the  $C_1$  to  $C_6$  range as can be seen from a typical product distribution plot (Figure VI-9).

SCHULZ-FLORY PRODUCT DISTRIBUTION

RUN NUMBER: 213-74B-2    ON-STREAM TIME: 145 HRS    ANALYSIS DATE: 06/10/81

TODAY'S DATE : 8/18/82



SLOPE  $b = -0.71425$     INTERCEPT  $a = -0.935898$   
 CORRELATION COEFFICIENT  $r = -0.956511$   
 SCHULZ-FLORY PROBABILITY  $\alpha = 0.489659$

FIGURE VI-8

MODIFIED SCHULZ-FLORY PROBABILITY PARAMETER VS. ON-STREAM TIME FOR UCI L-1122 CATALYST TESTED IN THE BERTY REACTOR

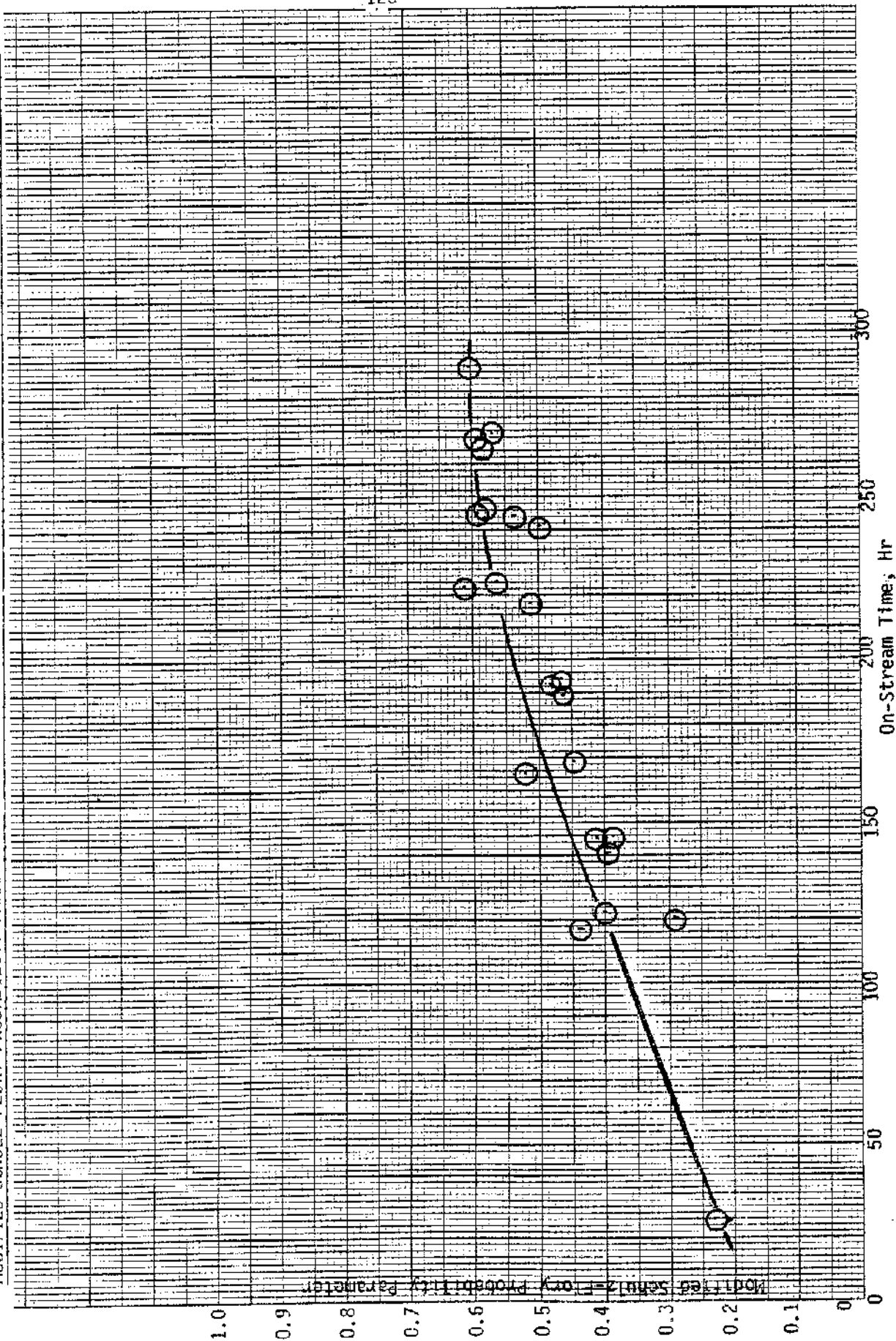
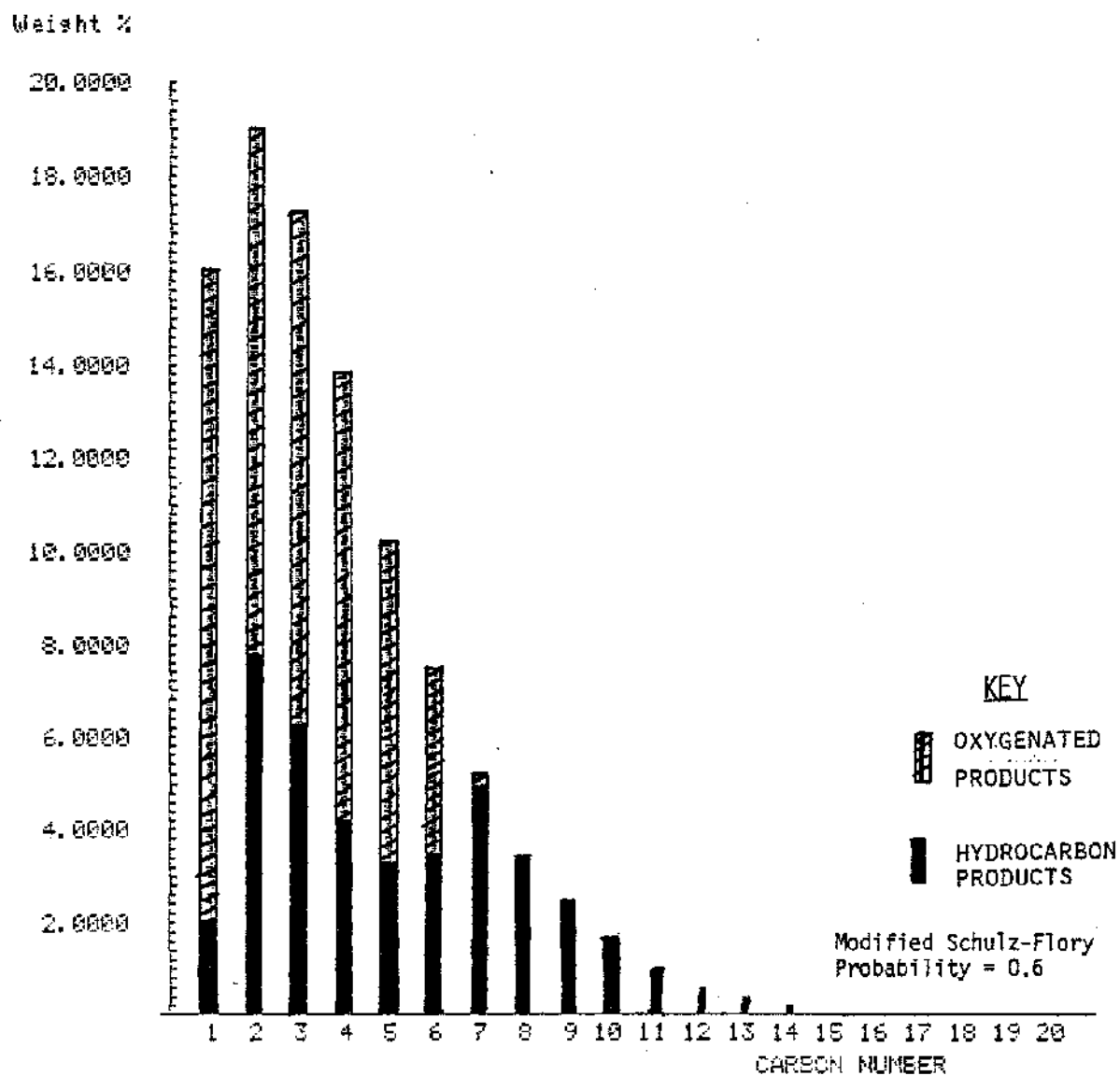


FIGURE VI-9

TYPICAL ALKANOLS SYNTHESIS PRODUCT DISTRIBUTION  
FOR UCI L-1122 CATALYST



• Effect of Synthesis Gas Composition

Although the product selectivities and ALKANOL compositions appeared to be stronger function of catalyst age and not operating conditions, the per pass carbon monoxide conversions were greatly influenced by synthesis gas compositions. At a fixed reactor severity and over the range of about 120-250 hours on-stream time, it appeared that hydrogen/carbon monoxide ratio had a significant effect on the value of carbon monoxide conversion (Figure VI-10). A cross-plot of hydrogen/carbon monoxide ratio vs. carbon monoxide conversion level (Figure VI-11) shows the almost linear effect (lower curve) of hydrogen/carbon monoxide ratio on carbon monoxide conversion over the range of 0.5/1 to 2/1 ratios of the synthesis gas feeds. The upper curve on the figure shows the total carbon monoxide conversion which reflects the additional conversion of carbon monoxide to carbon dioxide via the water-gas shift reaction. At the higher hydrogen/carbon monoxide ratios studied it can be seen that the carbon monoxide conversion via water-gas shift is not increasing with hydrogen/carbon monoxide ratio as rapidly as via alcohol (and hydrocarbon) formation.

Although the explicit role of carbon dioxide in the ALKANOLS synthesis reactions is not well understood, there appears to be a significant effect of carbon dioxide content of the synthesis feed gas on the per pass carbon monoxide conversions to alcohol and hydrocarbon products. Figure VI-12 indicates that for 2/1 hydrogen/carbon monoxide synthesis gases processed in the Berty backmixed reactor, there appears to be an optimal carbon dioxide content of the synthesis gas with respect to maximizing the carbon monoxide conversion to alcohol and hydrocarbon products. A recent notable paper (51) has concluded that for low pressure, Cu/ZnO type methanol synthesis catalysts, carbon dioxide levels of about 1-3 percent were required to maintain the optimal catalyst oxidation states on the catalyst surface. High carbon dioxide concentrations in the synthesis gas apparently lead to loss in active sites due to extensive adsorption of carbon dioxide on the catalyst surface. The data on Figure VI-12 suggest that the poisoning effect due to carbon dioxide adsorption may also be characteristic to the L-1122 ALKANOLS synthesis catalyst.

FIGURE VI-10

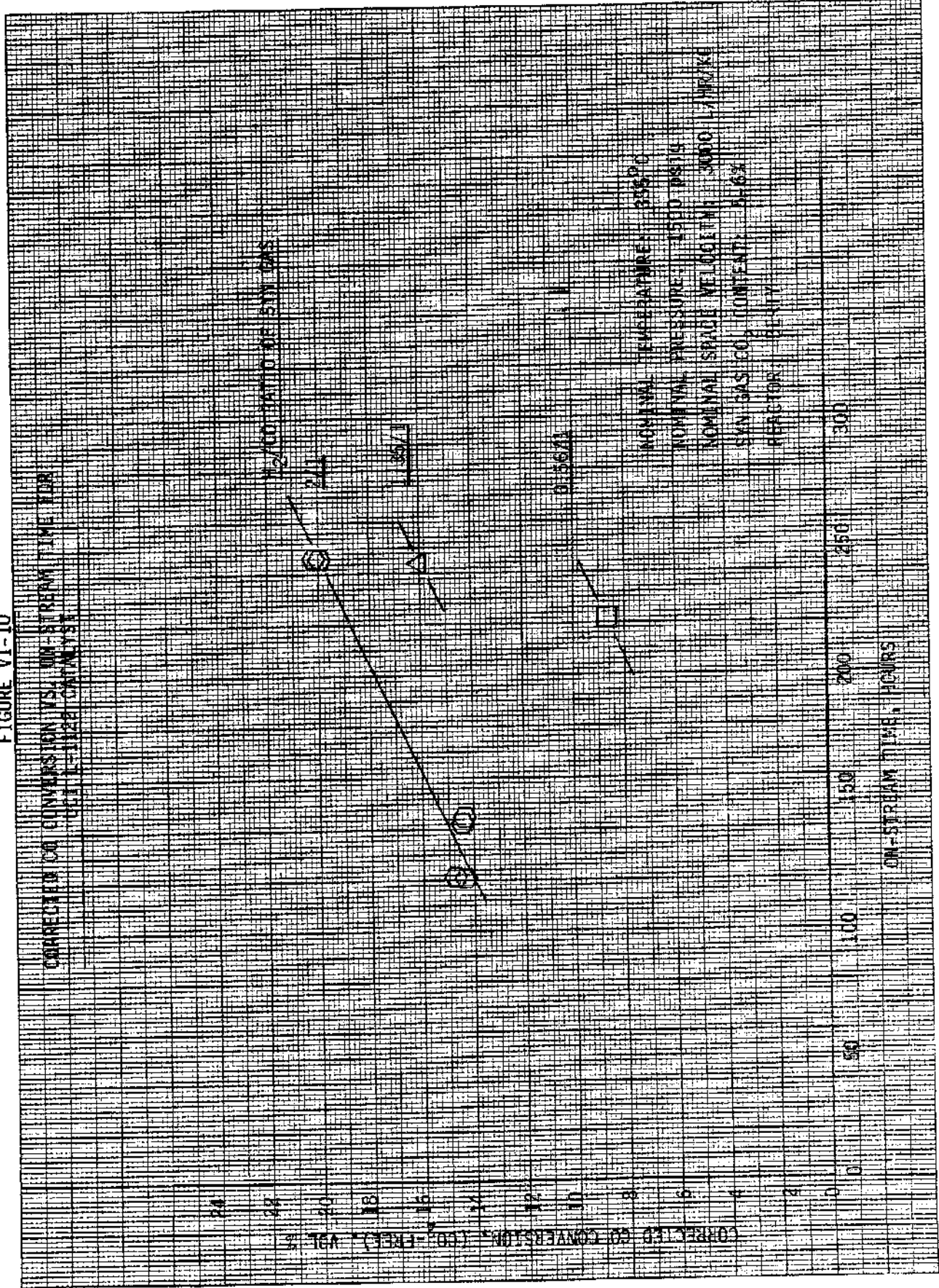




FIGURE VI-11  
CORRECTED CO CONVERSION VS. H<sub>2</sub>/CO MOLAR RATIO  
IN SYNTHESIS GAS FOR UCL-1-122 CATALYST

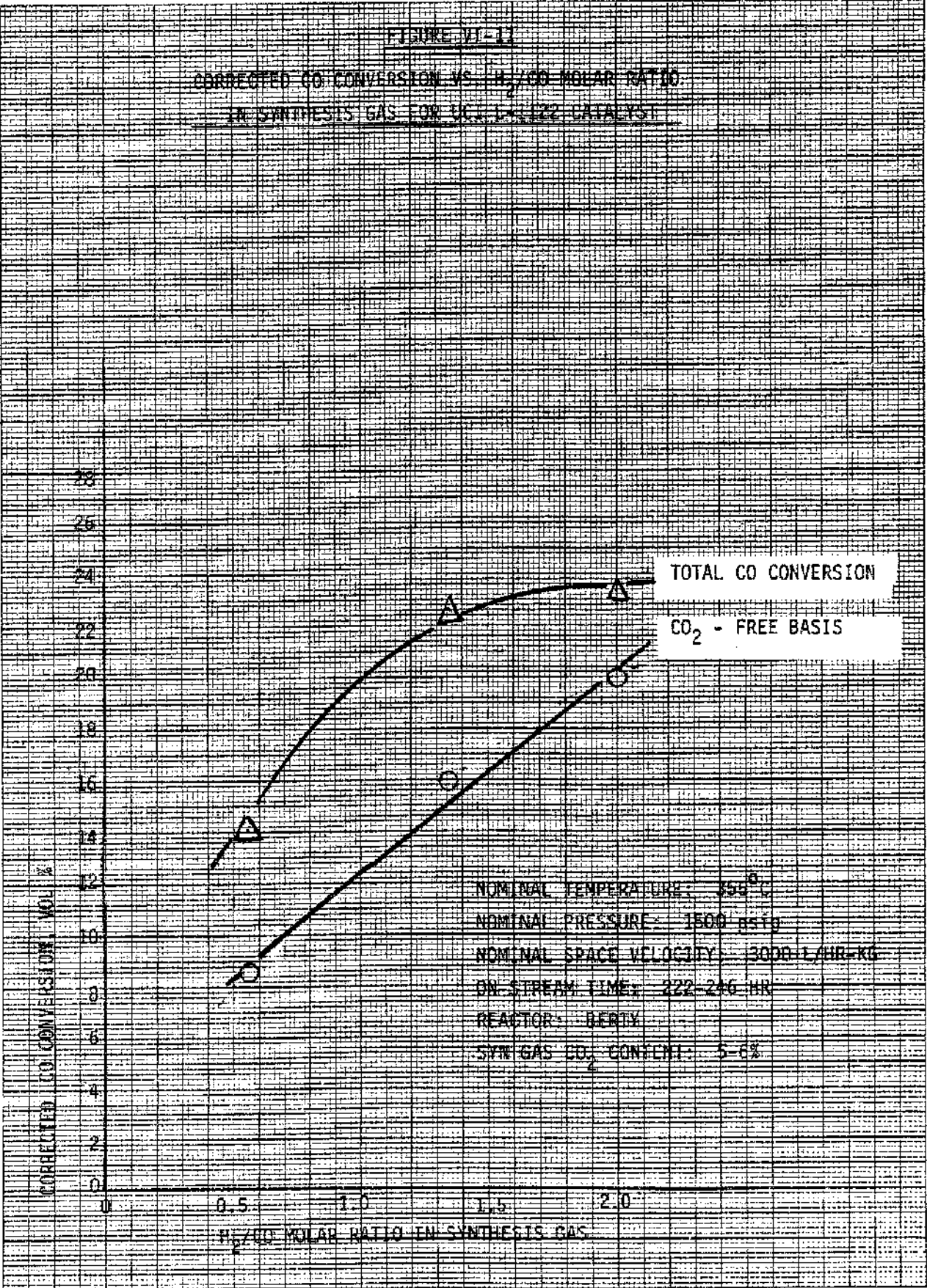
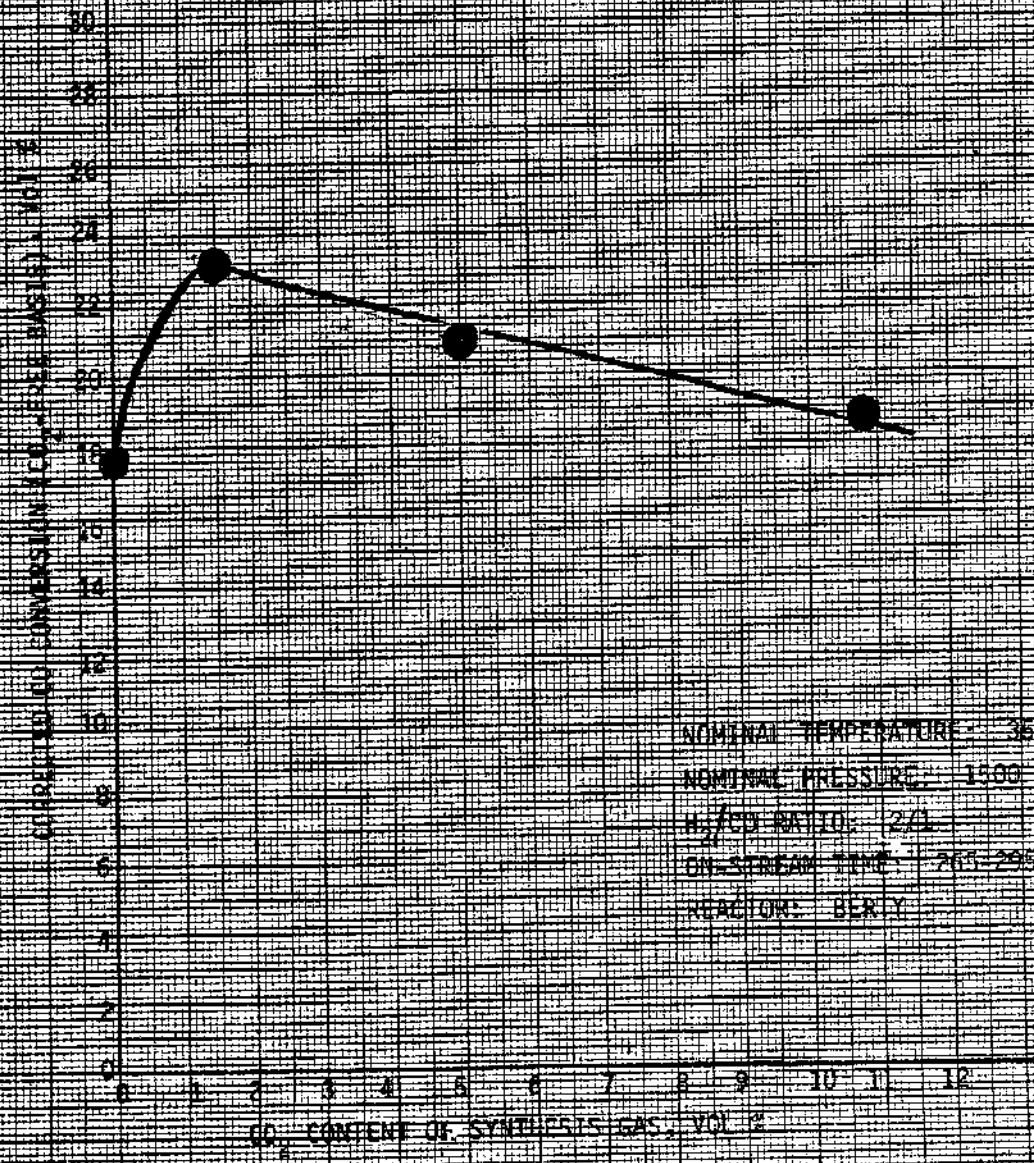


FIGURE VI-12  
CORRECTED CO CONVERSION VS. CO<sub>2</sub> CONTENT  
OF SYNTHESIS GAS FOR UO<sub>2</sub>LE-1122 CATALYST



NOMINAL TEMPERATURE: 365°C  
NOMINAL PRESSURE: 1500 PSIG  
H<sub>2</sub>/CO RATIO: 2/1  
ON-STREAM TIME: 265-295 HR  
REACTION: BERTY

• Effect of Space Velocity

The effect of space velocity on catalyst activity was difficult to quantify due to the effect of on-stream time (i.e., catalyst aging) on the performance of the catalyst. For the data correlated in Figure VI-13, increased space velocity was manifested as a decrease in carbon monoxide (carbon dioxide-free basis) conversion. Thus, doubling the space velocity from 2000 to 4000 SL/hr/kgm resulted in a 30 percent (relative) reduction in activity as measured by carbon monoxide conversion to alcohols and hydrocarbons. When activity was expressed as total carbon monoxide conversion including that controlled by the water-gas shift reaction, there appeared to be a poorer correlation between space velocity and activity. However, it is believed that this is a result of analytical inaccuracies related to the problems associated with the Carle gas chromatograph during this particular run.

b. Analysis of 298-Hour Campaign With Re-Reduced Catalyst

The L-1122 catalyst recovered after 292-hours on-stream time was inadvertently exposed to air during the sampling process. However, the balance of the catalyst was recharged to the Berty reactor and re-reduced according to the same procedure used for reducing the calcined sample. The initial data obtained after only a few hours on-stream time (see Table VI-3) indicated lower carbon monoxide conversion, lower ALKANOL selectivity and higher methanol content of ALKANOLS than those observed at the end of the first 292-hour campaign. With increasing on-stream time, however, it appeared that the catalyst was undergoing a continuing change in composition as manifested by the observed activity and product selectivity. Figure VI-14 shows the effect of catalyst aging as measured by cumulative on-stream time (first campaign as well as second campaign) on carbon monoxide conversion. The initial data point indicated a carbon monoxide conversion of about 11 percent (carbon dioxide-free basis) as compared to 19 percent at the end of the first test campaign. After the additional 298 hours on-stream time in campaign #2, the carbon monoxide conversion level appeared to line out at a value of about 16 percent (carbon dioxide-free basis).

FIGURE VI-13

EFFECT OF SPACE VELOCITY ON CO CONVERSION  
FOR UCLL-1122 CATALYST

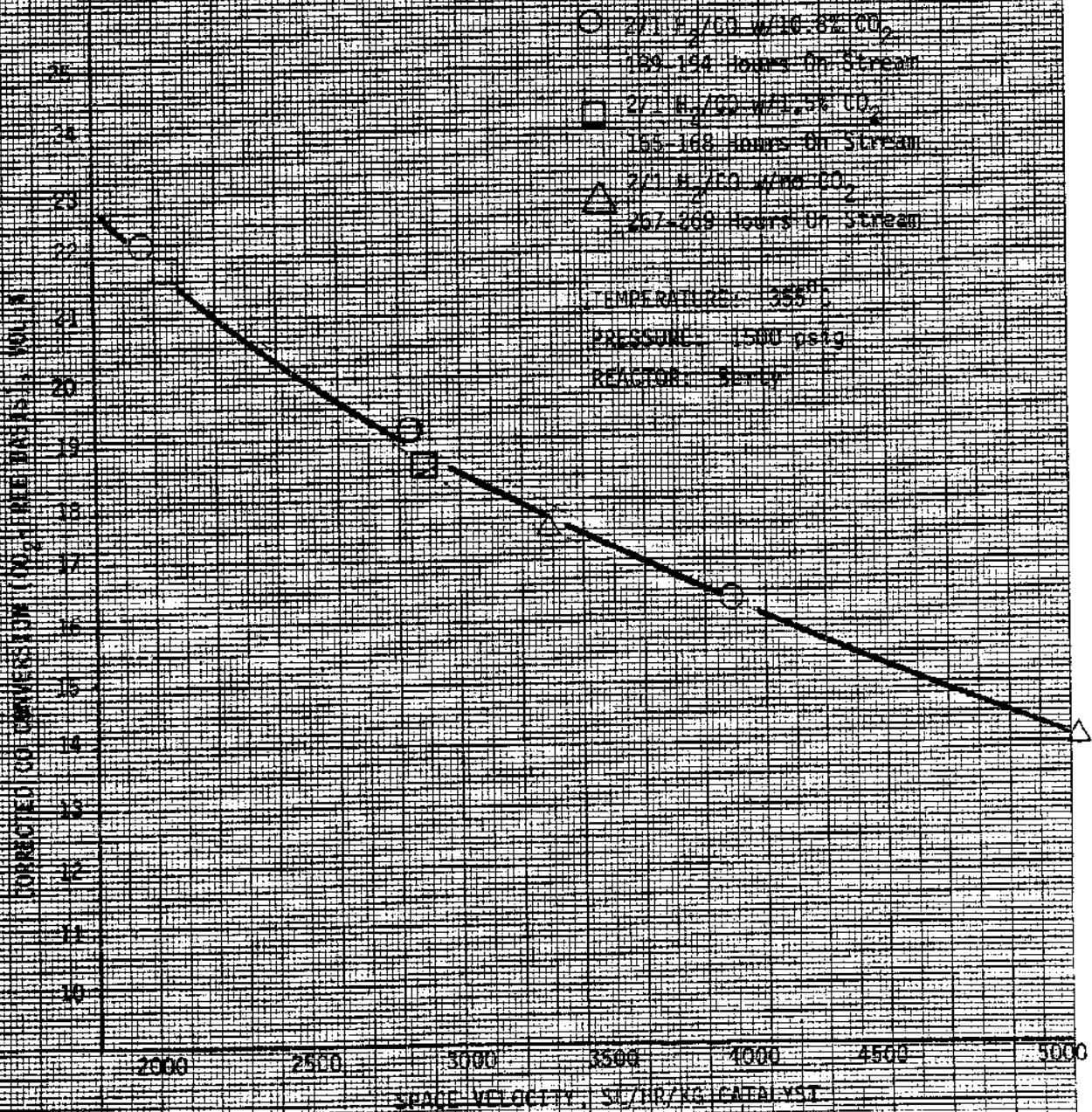
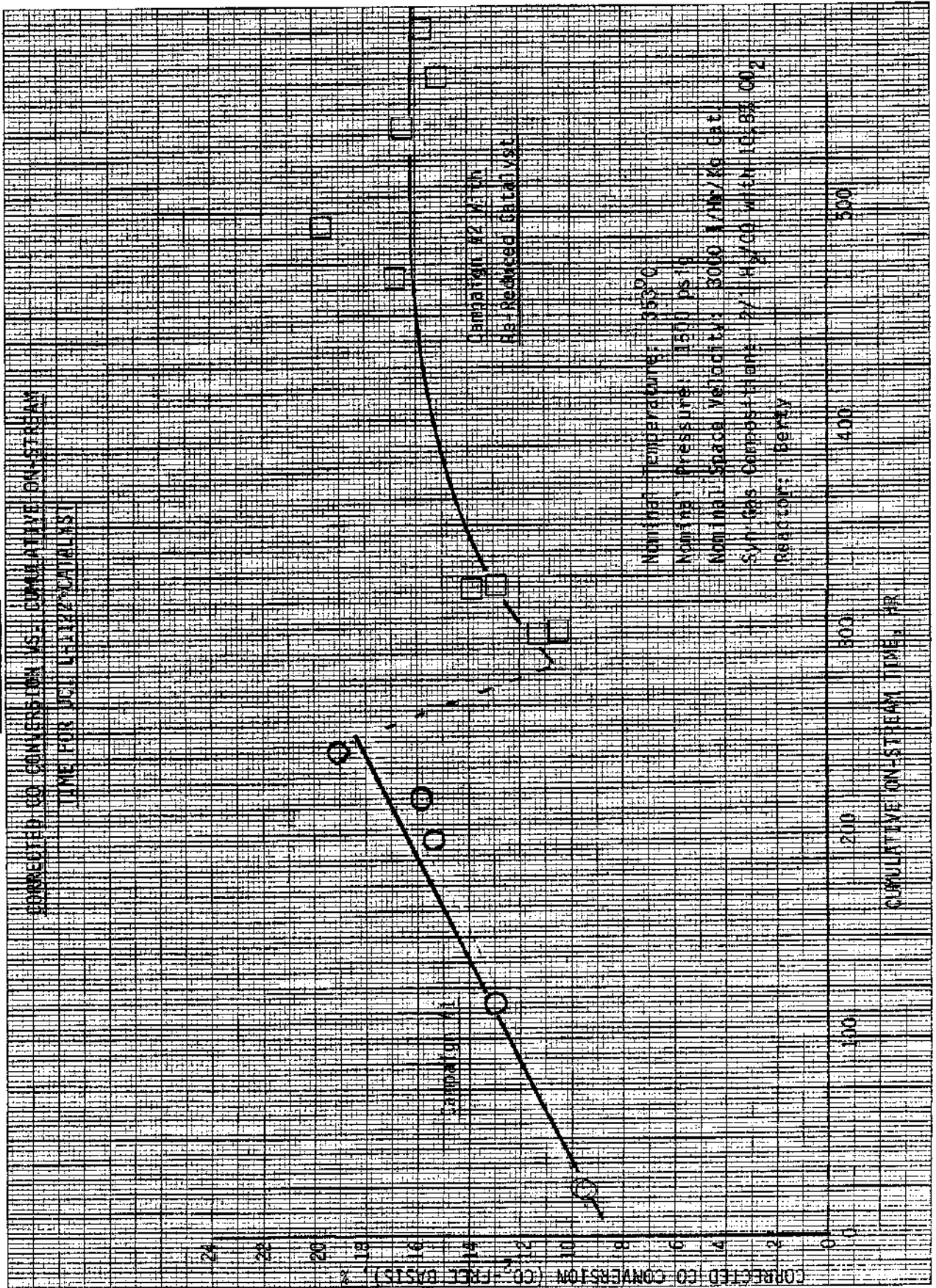




FIGURE VI-14



The total ALKANOLS selectivity for campaign #2 remained essentially constant over the 298-hour period at a value of about 72 weight percent with the remaining 28 percent attributable to light ( $C_1-C_3$ ) hydrocarbon gas formation. This value is somewhat lower than that of the ALKANOLS selectivity (85-90 percent) observed during the initial 292-hour campaign as shown in Figure VI-15. It appears that the exposure of the catalyst recovered at the end of the first 292-hour campaign to air may have irreversibly altered the catalyst composition in the direction of increasing light hydrocarbon gas formation.

The composition of the ALKANOLS mixture with cumulative on-stream time is shown in Figure VI-16. The plotted points represent the data for campaign #2 whereas the dotted lines represent the smoothed data (of Figures VI-4,5,6) for the first 292-hour campaign. Placing the re-reduced catalyst on synthesis gas service resulted in a significantly higher (62%) methanol content of the crude ALKANOLS mixture as compared to that (40%) at the end of the first campaign. However, on longer exposure time to synthesis gas, the methanol content decreased to a value of about 28 percent before lining out at about 34 percent at the end of the second 298-hour test campaign.

The  $C_4-C_9$  hydrocarbon content leveled off for most of the second campaign at a value of about 24 percent while the  $C_2-C_6$  oxygenates content leveled off at a value of about 42 percent. This ALKANOL composition together with the  $C_1-C_3$  hydrocarbon gas yield observed at the conclusion of the second test campaign is indicative of a modified Schulz-Flory distribution having a probability parameter of about 0.5 to 0.6. Thus, the increase in modified Schulz-Flory probability from an early value of 0.2 appears to have leveled off at the 0.5-0.6 value at the end of the 590 hours cumulative on-stream time (Figure VI-17). The resultant Schulz-Flory product distribution at the observed value of 0.5 for the modified Schulz-Flory probability parameter is shown in Figure VI-18. The calculated higher heating value of this crude ALKANOL mixture is 89,000 Btu/gal, which is equivalent to about 70 percent of that of

FIGURE VI-15

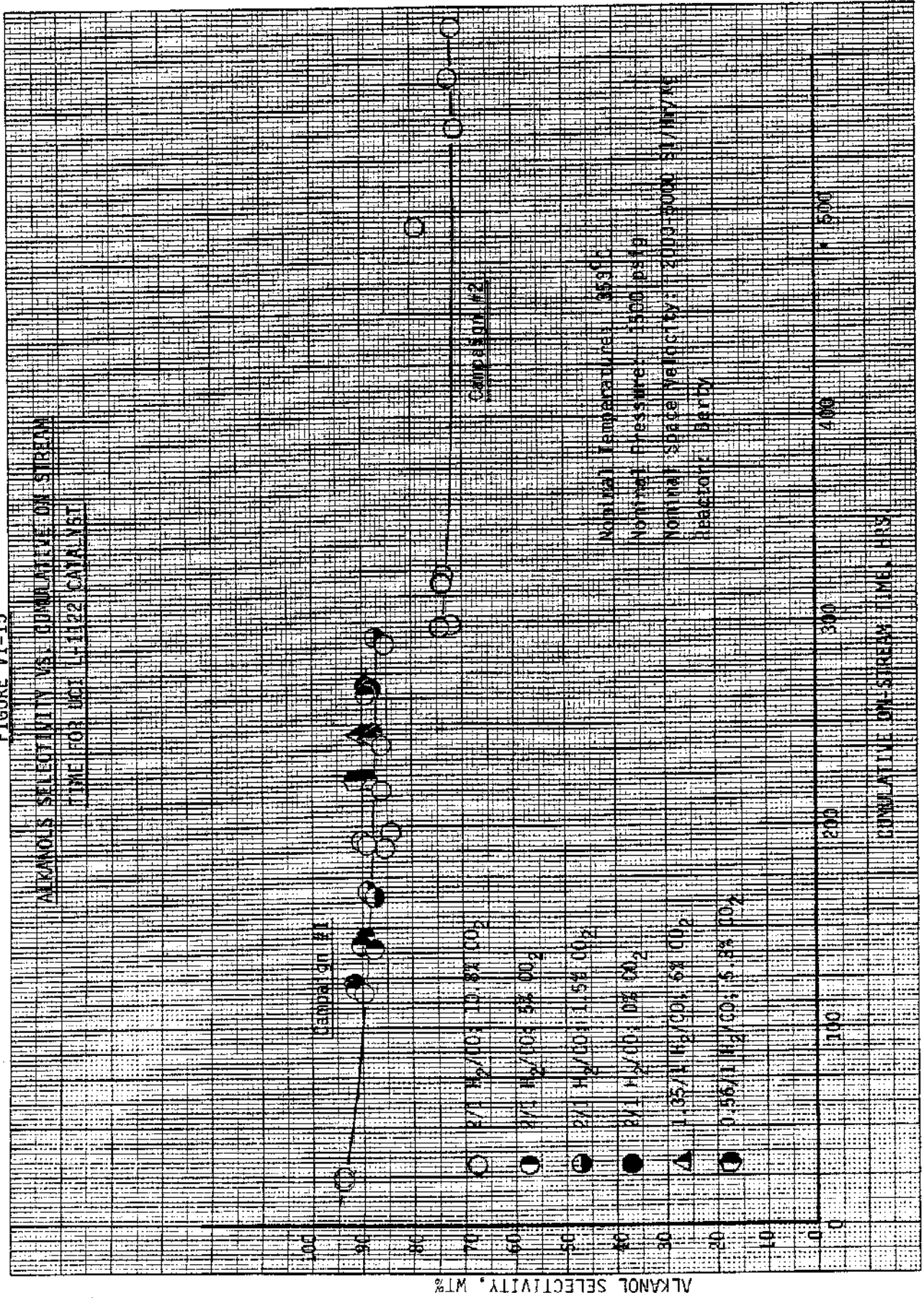




FIGURE VI-16

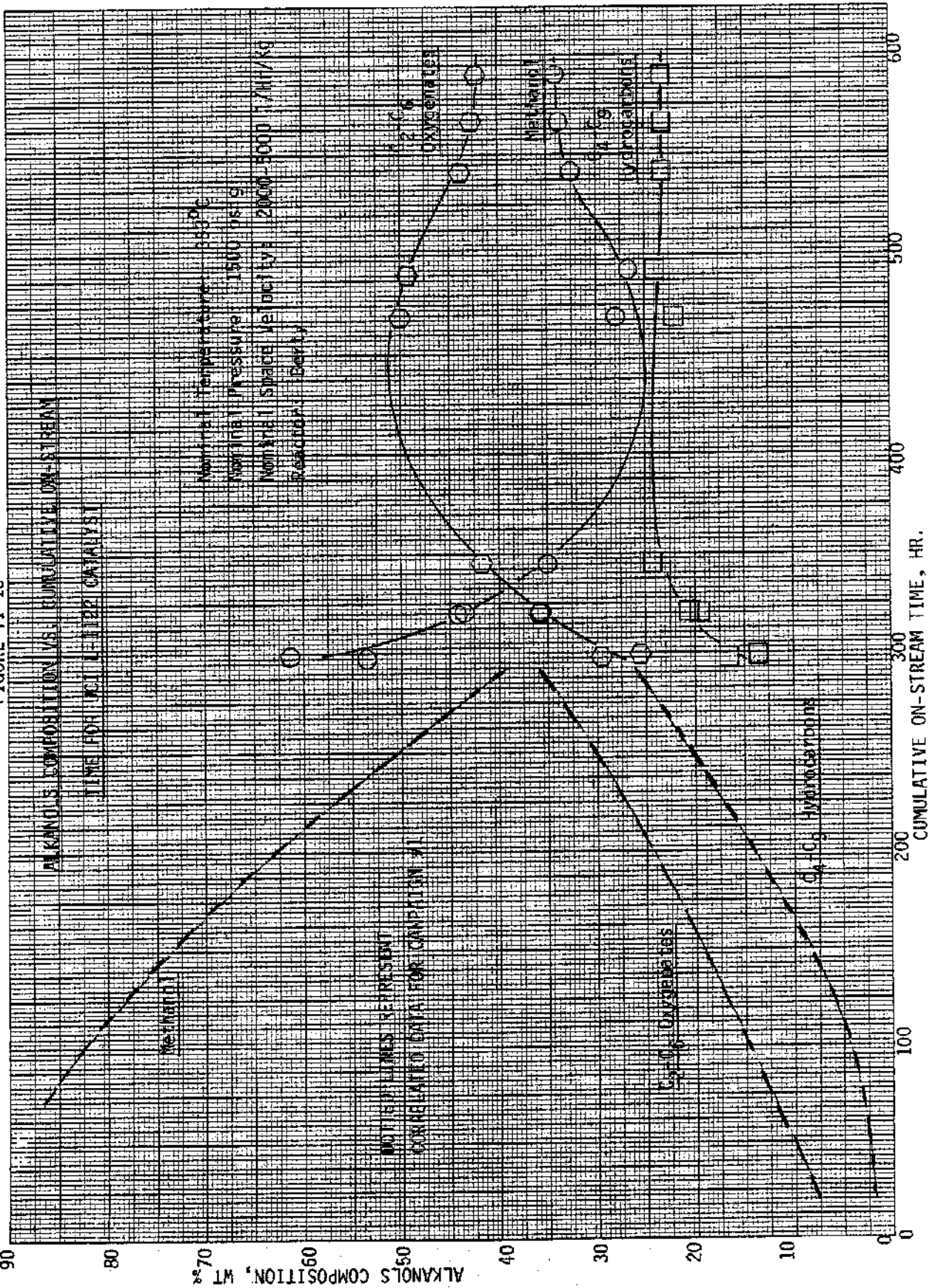


FIGURE VI-17

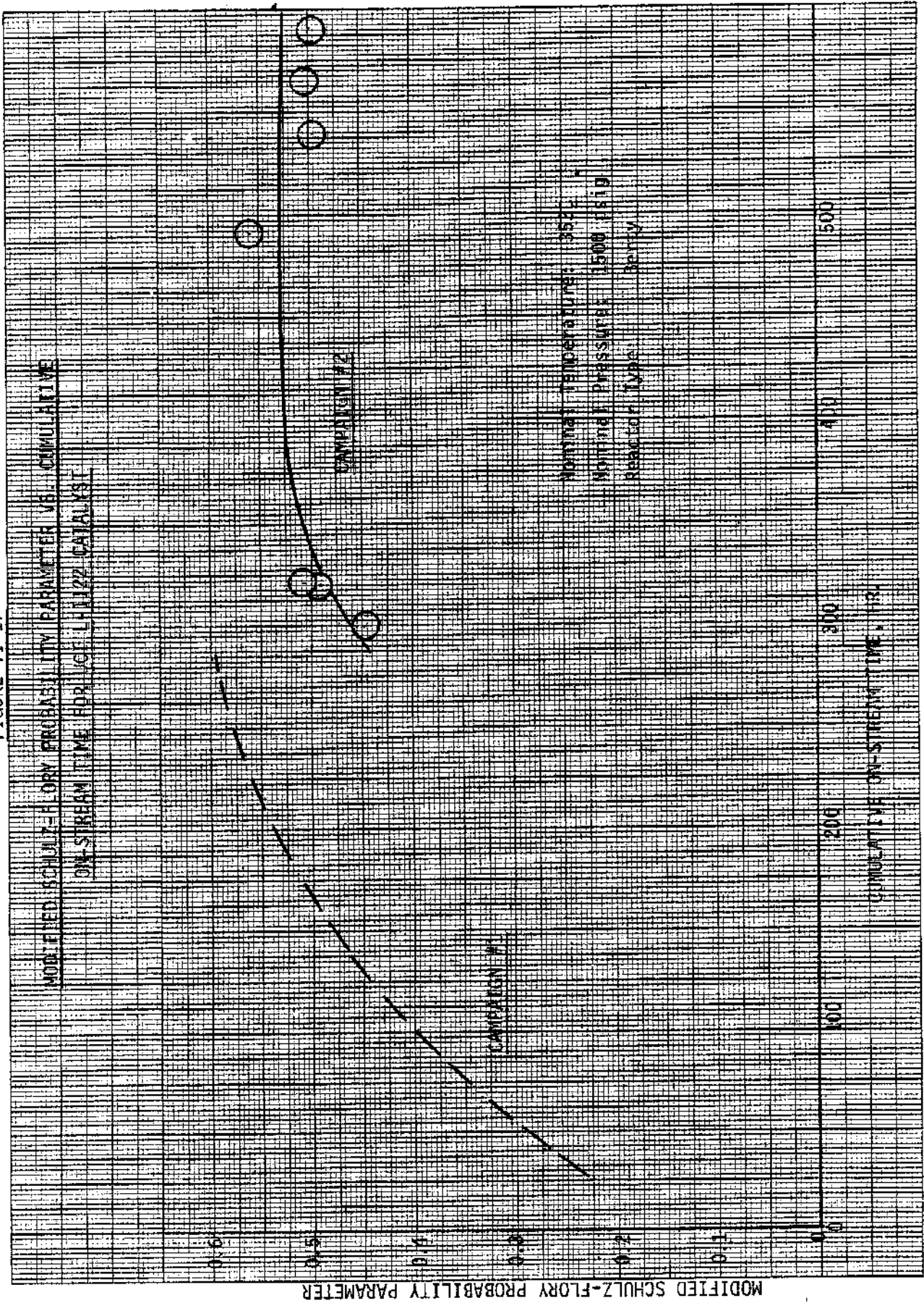
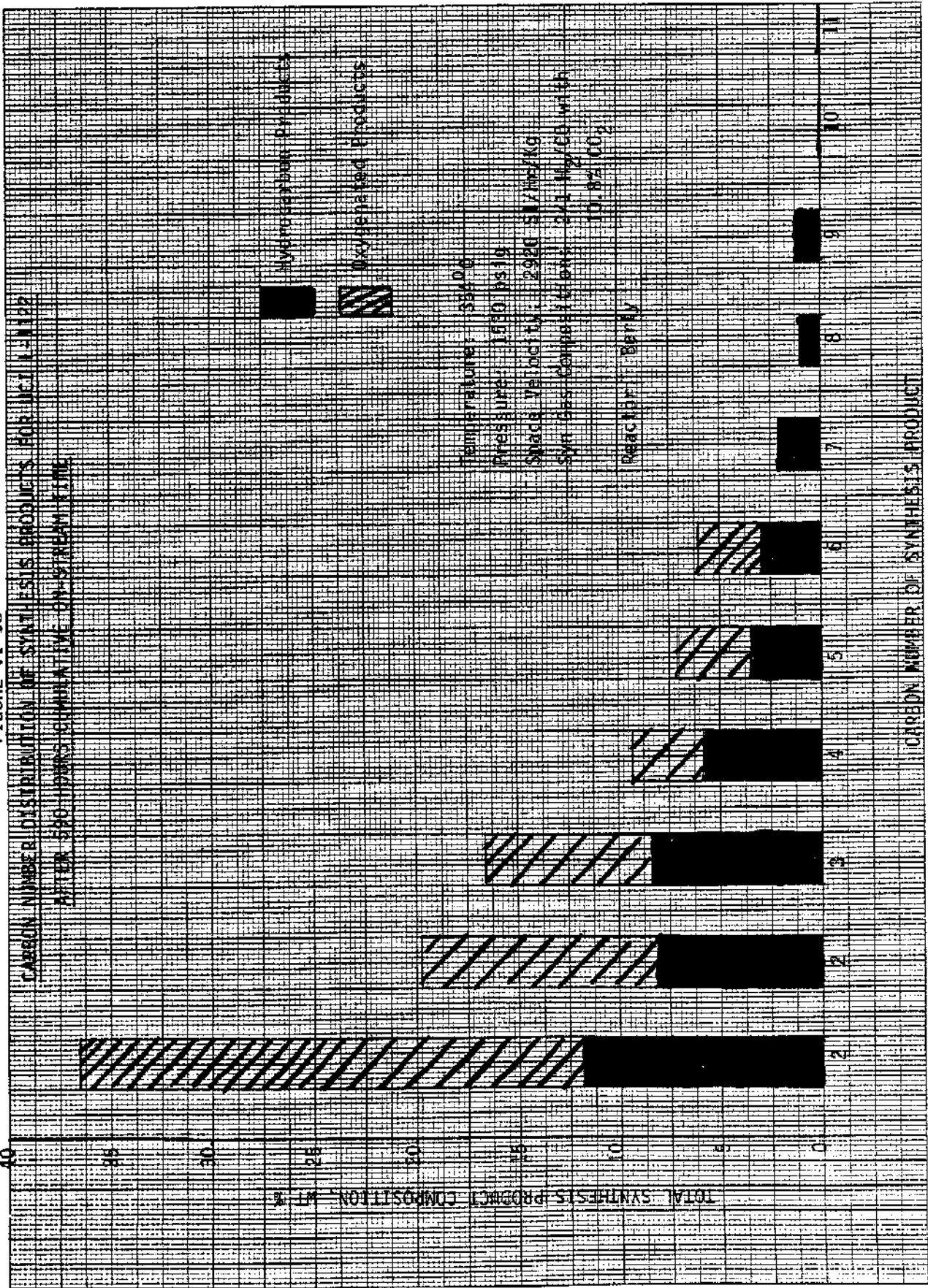


FIGURE VI-18



conventional gasoline. For comparison purposes, methyl fuel has a higher heating value (HHV) of about 50 percent of that of conventional gasoline. Thus, all other conditions constant, this ALKANOL fuel mixture will have a theoretical volumetric energy efficiency in an internal combustion engine 40 percent higher than that of methyl fuel.

A sample of UCI L-1122 catalyst taken after the initial 292-hour testing period was found to contain 5.0 percent carbon and 0.3 percent hydrogen. Three liquid product samples were taken during this period and analyzed for acid (as acetic acid) and aldehyde (as acetaldehydes) content. The results of these analyses are shown below:

<u>Hours On-Stream</u>	<u>Wt% Acids</u>	<u>Wt% Aldehydes</u>
0-145	0.12	0.13
145-194	0.28	0.12
194-292	0.37	0.11

2. UCI L-1123 Catalyst (Run #213-66P)

28.8 gms (25 cc) of UCI L-1123 calcined catalyst pellets were charged to the plug-flow reactor in a 2:1 volumetric dilution ratio with inert alumina beads (Rhodia SCS-9). The catalyst was activated by reduction with a 2 percent hydrogen/98 percent nitrogen gas at 1 atmosphere pressure and feed rate of 800-900 Sl/hr/kg catalyst. Reduction temperature was gradually increased from an initial temperature of 200°C, to a final temperature of 350°C over a 24-hour period. During the reduction, the uptake of hydrogen was monitored by gas chromatographic analysis, and the reduction was considered complete when the observed concentration of hydrogen in the effluent stream reached 2 percent. At this time, the feed gas was switched to high purity hydrogen for 3 hours, then purged with nitrogen before introducing synthesis gas.

A total of 183 hours of on-stream time were logged during this test. Three synthesis gas compositions were tested: 2/1 hydrogen/carbon monoxide with 10.8 percent carbon dioxide; 2/1 hydrogen/carbon monoxide with 5 percent carbon dioxide, and 1.35/1 hydrogen/carbon monoxide with 6

percent carbon dioxide. The system pressure was held at 1510 psig, and the temperature held at 354<sup>0</sup>C for the first 175 hours on-stream, at which time it was increased to 374<sup>0</sup>C. Table VI-8 summarizes the run conditions and results for the 17 material balance tests made with L-1123 catalyst. Table VI-9 shows the crude ALKANOL fuel distributions for each of the material balance tests made.

Figure VI-19 shows the apparent effect of catalyst on-stream time on activity as measured by per pass carbon monoxide conversion (carbon dioxide-free basis). Over the 183-hour test duration, catalyst deactivation was observed. The rate of conversion of synthesis gas to ALKANOLS as well as to light hydrocarbon gases was decreasing. There was a discernible effect of carbon dioxide content of the synthesis gas on the relative activities as depicted in the figure. At about 75 hours on-stream time, increasing the carbon dioxide content of the synthesis gas from 5 percent to about 10.8 percent resulted in a decreased activity equivalent to about 4 carbon monoxide percentage conversion points. This represents a relative decrease of about 20 percent, which is almost equivalent to the similar effect of increasing the space velocity from 2000 to 3000 SL/hr/kg.

Over the bulk of the test, the ALKANOLS and light hydrocarbon gas selectivities remained essentially constant as seen in Figure VI-20. Also, the ALKANOLS composition showed essentially the same trend (Figure VI-21). Just after the tests to evaluate the effect of operating at 375<sup>0</sup>C reaction temperature, a precipitous drop in the selectivities to ALKANOLS, and to the methanol component in particular, was observed. ALKANOLS selectivities decreased from about 86 percent to about 60 percent after returning to the 353<sup>0</sup>C reaction temperature level from the higher temperature evaluation tests. A corresponding increase in the C<sub>1</sub>-C<sub>3</sub> hydrocarbon gas selectivity was noted. The C<sub>2</sub>-C<sub>6</sub> oxygenates and the C<sub>4</sub>-C<sub>9</sub> hydrocarbons selectivities increased to match the decline in the methanol selectivity.

**SUMMARY FOR RUN # 213-66P**

TODAY'S DATE : 07/16/81

CATALYST NUMBER : UCI L-1123  
 ATOMIC FORMULA :  
 PREP. METHOD : UCI PREP  
 SURFACE AREA(1) : 0 m<sup>2</sup>/gm  
 BULK DENSITY(1) : 1.15 gm/cc

TEST NUMBER	1	2	3	4	5	6
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TEST CONDITIONS :

FEED H <sub>2</sub> /CO Ratio	2.11	2.11	2.13	2.13	2.14	2.14
FEED CO <sub>2</sub>	4.96	4.96	18.94	18.94	18.98	18.98
AVE. TEMP., °C	352.0	353.0	355.0	356.0	355.0	356.0
HOT SPOT, °C	352.0	354.0	355.0	356.0	355.0	356.0
PRESSURE, psig	1505.0	1505.0	1510.0	1510.0	1510.0	1505.0
WHSV, l/hr/kgm cat.	2177.7	2193.0	2857.0	2961.9	3028.3	3043.4
HOURS on STREAM	3.3	5.0	73.0	75.5	97.5	100.3

CONVERSION :

CO to Prods., vol%	20.02	20.68	14.08	11.13	10.15	9.62
CO to CO <sub>2</sub> , vol%	7.31	6.63	1.48	0.26	-0.16	0.50
CO, gm mol/hr/kgm cat.	7.25	7.29	3.43	3.61	3.24	3.30
STY of Oxygenates(2) gm mol/hr/kgm cat.	4.82	5.00	2.37	2.61	2.18	2.28

STOICHIOM. H <sub>2</sub> /CO converted	1.60	1.62	1.96	1.87	1.93	1.81
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CARBON SELECTIVITY (Normalized Mol % on CO<sub>2</sub>-free Basis) :

CH <sub>3</sub> OH	50.15	51.33	55.95	59.41	57.52	57.57
C <sub>2</sub> -C <sub>6</sub> ALCOHOLS	13.48	14.46	10.00	9.15	7.86	8.45
C <sub>2</sub> -C <sub>6</sub> ALD. & ESTERS	2.81	2.71	2.42	3.57	1.66	3.04
CH <sub>4</sub>	15.60	15.36	14.99	13.16	13.16	13.06
C <sub>2</sub> -C <sub>3</sub> HYDROCARBONS	10.20	9.25	8.83	8.23	8.48	8.42
C <sub>4</sub> + HYDROCARBONS	7.67	6.90	7.01	6.47	11.31	9.47

APPROACH TO(3)

WGS Equilibrium, °C :				-52.3	-47.2	-33.5
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CARBON ACCOUNTABILITY, % (4):	119.3	111.2	159.9	111.4	114.5	122.6
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OXYGEN REJECTION RATIO, (5):				0.03	0.03	0.02
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(1) Fresh, non-reduced catalyst.

(2) Space Time Yield (STY) =  $WHSV/22.4 * \%CO \text{ in feed}/100 * \%CO \text{ conv.}/100 * \%Sel. \text{ to Oxygenates}/100$ .

(3) Defined as  $T = T_{eq} - T_{hs}$   
 where  $T_{eq}$  = water gas shift equilibrium temp calculated for reactor eff. composition.  
 $T_{hs}$  = hot spot temperature.

(4) Defined as Carbon observed in Products to Feed Carbon converted.

(5) Defined as ratio of oxygen removed as water to that removed as CO<sub>2</sub>.

Continued...



Table VI-8 (Continued)

## SUMMARY FOR RUN # 213-66P

=====						
						TODAY'S DATE : 07/16/81
-----						
CATALYST NUMBER :	UCI L-1123					
ATOMIC FORMULA :						
PREP. METHOD :	UCI PREP					
SURFACE AREA(1) :	0	m <sup>2</sup> /gm				
BULK DENSITY(1) :	1.15	gm/cc				
TEST NUMBER	7	8	9	10	11	12
-----						
TEST CONDITIONS :						
FEED H <sub>2</sub> /CO Ratio	2.13	2.12	2.15	2.15	2.19	1.49
FEED CO <sub>2</sub>	10.86	5.04	10.94	5.28	11.03	6.37
AVE. TEMP., °C	356.0	356.0	352.0	353.0	352.0	355.0
HOT SPOT, °C	356.0	356.0	352.0	353.0	352.0	355.0
PRESSURE, psia	1505.0	1505.0	1505.0	1505.0	1505.0	1505.0
WHSV, 1/hr/kgm cat.	3004.8	3176.6	3015.0	2146.1	2058.5	1974.4
HOURS on STREAM	121.4	123.7	144.5	147.3	170.5	173.5
CONVERSION :						
CO to Prods., vol%	9.27	11.60	9.94	15.12	13.60	8.55
CO to CO <sub>2</sub> , vol%	0.99	2.11	-0.14	2.65	1.05	3.05
CO, gm mol/hr/kgm cat.	3.40	5.30	3.14	4.57	3.17	3.27
STY of Oxygenates(2)						
gm mol/hr/kgm cat.	2.30	3.90	2.19	3.41	2.20	2.40
STOICHIOM. H <sub>2</sub> /CO converted	1.08	1.70	2.00	1.73	1.97	1.66
CARBON SELECTIVITY (Normalized Mol % on CO <sub>2</sub> -free Basis) :						
CH <sub>3</sub> OH	58.61	61.96	60.83	59.99	55.66	58.61
C <sub>2</sub> -C <sub>6</sub> ALCOHOLS	7.40	9.88	7.59	11.87	10.01	11.12
C <sub>2</sub> -C <sub>6</sub> ALD. & ESTERS	1.62	3.36	1.50	2.75	3.65	3.47
CH <sub>4</sub>	15.41	11.32	13.74	11.14	12.45	11.23
C <sub>2</sub> -C <sub>3</sub> HYDROCARBONS	10.14	7.31	9.49	7.61	9.25	8.13
C <sub>4</sub> + HYDROCARBONS	6.75	6.17	6.85	6.65	8.98	7.44
APPROACH TO(3)						
WGS Equilibrium, °C :	-80.9	-50.6	-39.9	-40.4	-75.6	
CARBON ACCOUNTABILITY, % (4):	111.6	104.2	105.2	106.3	124.7	155.0
OXYGEN REJECTION RATIO, (5):	0.02	0.03	0.03	0.03	0.02	
-----						

(1) Fresh, non-reduced catalyst.

(2) Space Time Yield (STY) =  $\text{WHSV}/22.4 * \% \text{CO in feed}/100 * \% \text{CO conv.}/100 * \% \text{Sel. to Oxygenates}/100$ .(3) Defined as  $T = T_{eq} - T_{hs}$ where  $T_{eq}$  = water gas shift equilibrium temp calculated for reactor eff. composition. $T_{hs}$  = hot spot temperature.

(4) Defined as Carbon observed in Products to Feed Carbon converted.

(5) Defined as ratio of oxygen removed as water, to that removed as CO<sub>2</sub>.



**SUMMARY FOR RUN # 213-66F**

TODAY'S DATE : 07/16/81					
CATALYST NUMBER : UCI L-1123					
ATOMIC FORMULA :					
PREP. METHOD : UCI PREP					
SURFACE AREA(1) :	0	m <sup>2</sup> /gm			
BULK DENSITY(1) :	1.15	gm/cc			
TEST NUMBER	13	14	15	16	17
TEST CONDITIONS :					
FEED H <sub>2</sub> /CO Ratio	2.20	2.13	2.13	2.14	2.14
FEED CO <sub>2</sub>	10.87	10.90	10.90	10.93	10.93
AVE. TEMP., °C	351.0	374.0	374.0	353.0	353.0
HOT SPOT, °C	351.0	374.0	374.0	353.0	353.0
PRESSURE, psia	1515.0	1510.0	1510.0	1510.0	1510.0
WHSV, 1/hr/kam cat.	2083.1	2958.8	2878.5	1928.2	1924.6
HOURS on STREAM	175.5	181.0	179.5	181.0	183.3
CONVERSION :					
CO to Prods., vol%	9.53	8.72	8.59	10.38	10.28
CO to CO <sub>2</sub> , vol%	1.95	2.73	2.65	2.84	1.86
CO, gm mol/hr/kam cat.	2.52	3.65	3.47	2.73	2.58
STY of Dioxenates(2)					
gm mol/hr/kam cat.	1.86	2.08	1.24	1.22	0.98
STOICHIOM. H <sub>2</sub> /CO converted	1.68	1.73	1.81	1.66	1.77
CARBON SELECTIVITY (Normalized Mol % on CO <sub>2</sub> -free Basis) :					
CH <sub>3</sub> OH	58.65	42.42	23.23	38.63	25.20
C <sub>2</sub> -C <sub>6</sub> ALCOHOLS	12.11	10.90	9.53	18.60	11.62
C <sub>2</sub> -C <sub>6</sub> ALD. & ESTERS	3.20	3.70	2.95	3.54	2.25
CH <sub>4</sub>	11.07	19.10	32.94	27.09	29.49
C <sub>2</sub> -C <sub>3</sub> HYDROCARBONS	7.53	11.41	20.57	16.31	19.98
C <sub>4</sub> + HYDROCARBONS	7.44	12.50	10.79	11.83	11.45
APPROACH TO(3)					
WGS Equilibrium, °C :	0.0	0.0	-71.1	-35.6	-2.1
CARBON ACCOUNTABILITY, % (4):	128.4	139.9	128.8	182.9	92.5
OXYGEN REJECTION RATIO, (5):			0.03	0.04	0.06

(1) Fresh, non-reduced catalyst.

(2) Space Time Yield (STY) =  $WHSV/22.4 * \%CO \text{ in feed}/100 * \%CO \text{ conv.}/100 * \%Sel. \text{ to Dioxenates}/100$ .

(3) Defined as  $T = T_{ea} - T_{hs}$

    where  $T_{ea}$  = water gas shift equilibrium temp calculated for reactor eff. composition.

$T_{hs}$  = hot spot temperature.

(4) Defined as Carbon observed in Products to Feed Carbon converted.

(5) Defined as ratio of oxygen removed as water, to that removed as CO<sub>2</sub>.

Table VI-9

CRUDE ALKANOL FUEL WI DISTRIBUTION  
RUN 213-66

Catalyst Number : UCI L-1123

Date : 4/24/81

Catalyst Formulation: Proprietary

Wt% (H<sub>2</sub>O FREE)

COMPONENT	TEST #					
	1	2	3	4	5	6
METHANOL	79.250	79.118	83.219	84.738	83.879	83.582
ETHANOL	3.371	3.363	3.154	2.717	2.657	2.671
N-PROP OL	4.397	4.538	3.308	2.802	2.488	2.613
N-BUT OL	4.474	5.270	3.088	2.643	2.192	1.934
N-PENT OL	.000	.277	.262	.121	.000	.256
N-HEX OL	.561	.386	.304	.000	.000	.296
ACET ALD	.000	.000	.000	.000	.000	.000
PROP ALD	.815	.183	.216	.797	.773	.842
BUT ALD	.923	.681	.805	.396	.320	.314
PENT ALD	.210	.650	.513	.945	.000	.874
HEX ALD	.550	.756	.447	.687	.296	.436
C4 H.C.	1.948	1.645	1.815	1.753	1.804	1.853
C5 H.C.	1.011	.908	.697	1.088	1.173	1.463
C6 H.C.	1.103	.921	.641	.472	1.274	1.373
C7 H.C.	.794	1.071	.820	.687	1.185	1.162
C8 H.C.	.279	.072	.425	.157	1.013	.331
C9 H.C.	.313	.161	.286	.000	.948	.000
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000
METHANOL	79.250	79.118	83.219	84.738	83.879	83.582
C2 - C6 ALCOHOLS	12.804	13.834	10.116	8.282	7.336	7.770
OTHER C2 - C6 OXYGENATES	2.498	2.270	1.981	2.824	1.389	2.465
C4 - C9 HYDROCARBONS	5.448	4.778	4.684	4.156	7.396	6.182
CALCULATED HIGHER HEATING VALUE Btu/gal	71904.	71983.	70422.	69719.	70730.	70558.

Continued...

Table VI-9 (Continued)

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 213-66

Catalyst Number : UCI L-1123

Date : 4/24/81

Catalyst Formulation: Proprietary

Wt% (H<sub>2</sub>O FREE)

COMPONENT	TEST #					
	7	8	9	10	11	12
METHANOL	86.924	85.042	87.274	83.414	81.784	82.629
ETHANOL	2.829	2.671	2.872	2.889	3.053	3.092
N-PROP OL	2.665	3.136	2.563	3.716	3.124	3.176
N-BUT OL	1.517	2.579	1.459	2.582	2.418	3.109
N-PENT OL	.150	.204	.145	.307	.270	.148
N-HEX OL	.000	.000	.000	.801	.417	.343
ACET ALD	.000	.000	.000	.000	.000	.000
PROP ALD	.991	.674	.858	.658	.948	.916
BUT ALD	.246	.418	.237	.440	.662	.726
PENT ALD	.000	.999	.000	.600	.878	.723
HEX ALD	.171	.465	.164	.436	.511	.420
C4 H.C.	2.279	1.549	2.192	1.670	2.369	1.949
C5 H.C.	.861	.585	.828	.628	.956	.786
C6 H.C.	.441	.499	.565	.525	.878	.650
C7 H.C.	.513	1.045	.657	1.134	1.123	.924
C8 H.C.	.195	.132	.187	.199	.349	.192
C9 H.C.	.219	.000	.000	.000	.261	.215
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000

METHANOL	86.924	85.042	87.274	83.414	81.784	82.629
C2 - C6 ALCOHOLS	7.162	8.591	7.038	10.296	9.282	9.868
OTHER C2 - C6 OXYGENATES	1.408	2.555	1.259	2.134	2.998	2.785
C4 - C9 HYDROCARBONS	4.507	3.812	4.429	4.156	5.937	4.717

CALCULATED HIGHER HEATING VALUE						
Btu/gal	7	8	9	10	11	12
	68783.	69574.	68644.	70269.	71112.	70559.

Table VI-9 (Concluded)

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 213-66

Catalyst Number : UCI L-1123

Date : 4/24/81

Catalyst Formulation: Proprietary

Wt% (H<sub>2</sub>O FREE)

COMPONENT	TEST #				
	13	14	15	16	17
METHANOL	81.926	74.467	64.657	68.400	64.362
ETHANOL	3.703	4.146	6.906	5.920	8.105
N-PROP OL	4.025	4.345	5.067	5.148	5.386
N-BUT OL	2.582	3.096	5.092	3.922	5.658
N-PENT OL	.472	.142	.000	.222	.000
N-HEX OL	.000	.328	.000	.000	.000
ACET. ALD	.295	.354	.550	.555	.439
PROP ALD	1.323	.467	1.088	.732	.771
BUT ALD	.483	.927	2.252	1.635	1.436
PENT ALD	.115	1.246	.538	1.085	.000
HEX ALD	.403	.644	.313	.505	.665
C4 H.C.	1.790	2.614	7.075	4.830	6.363
C5 H.C.	.869	.927	2.928	2.362	2.872
C6 H.C.	.692	2.353	1.883	1.302	1.715
C7 H.C.	.671	1.931	1.251	1.514	.997
C8 H.C.	.306	.367	.000	.575	.379
C9 H.C.	.344	1.648	.400	1.292	.851
TOTAL	100.000	100.000	100.000	100.000	100.000
METHANOL	81.926	74.467	64.657	68.400	64.362
C2 - C6 ALCOHOLS	10.783	12.057	17.065	15.212	19.149
OTHER C2 - C6 OXYGENATES	2.619	3.637	4.742	4.512	3.311
C4 - C9 HYDROCARBONS	4.672	9.839	13.537	11.876	13.178
CALCULATED HIGHER HEATING VALUE Btu/#1	70503.	74432.	77402.	76329.	77459.

FIGURE VI-19

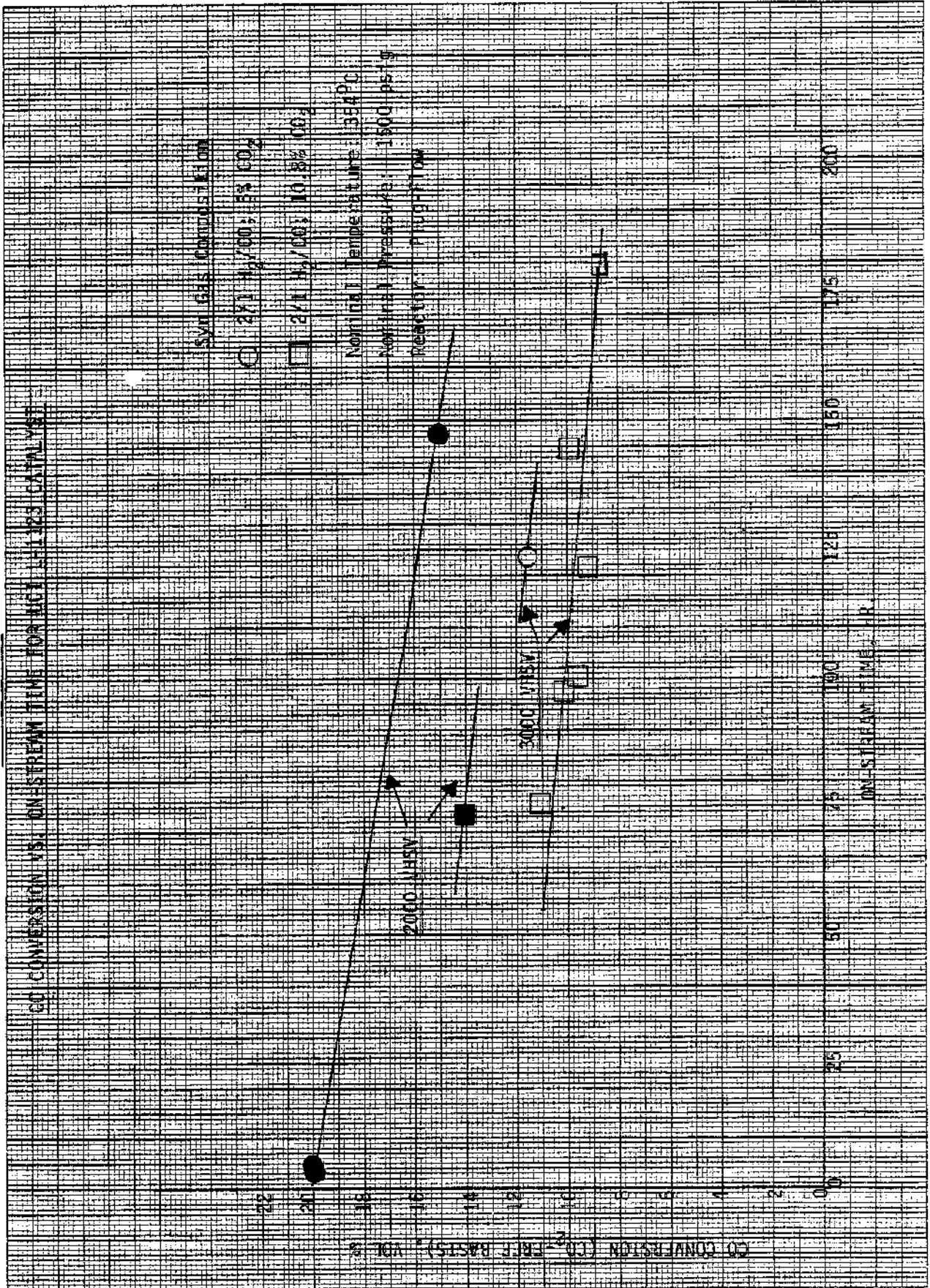


FIGURE VI-20

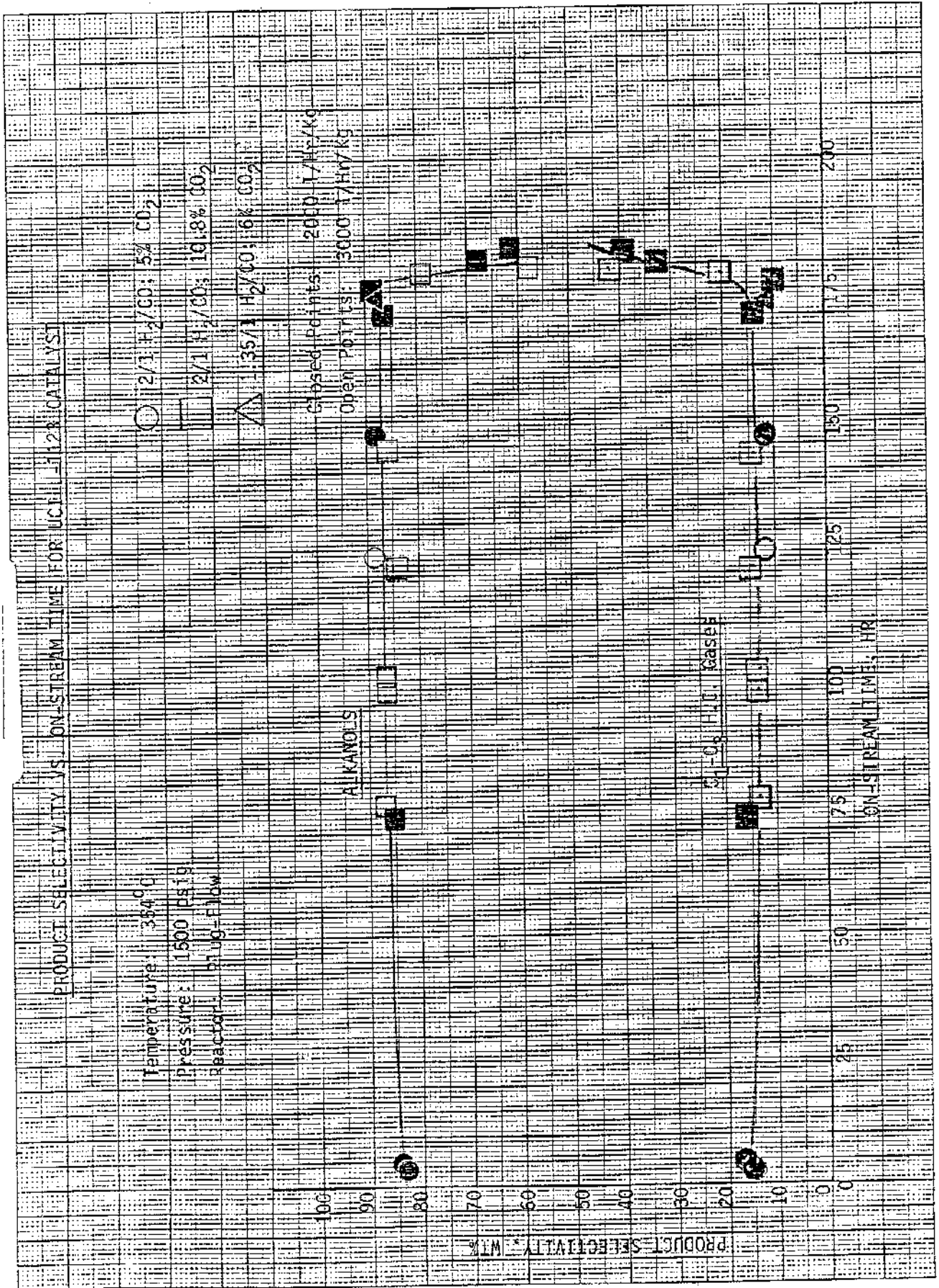


FIGURE VI-21  
 CRUDE ALKANOL DISTRIBUTION VS. ON-STREAM TIME FOR LCI L-1123 CATALYST

