Unlike the results observed for L-1122 catalyst tested in the Berty reactor, the modified Schulz-Flory probability parameter for L-1123 catalyst showed essentially no variation with catalyst on-stream time (Figure VI-22). The probability parameter remained essentially constant at a value of about 0.4. This lower value indicates that L-1123 catalyst does not demonstrate similar activities for the polymerization of alcohols (and hydrocarbons) as those observed for L-1122 catalyst. In fact, L-1123 catalyst produces essentially a crude methanol product containing about 15 percent higher alcohol (and hydrocarbon) components. This is shown graphically in Figure VI-23 where the synthesis product distribution observed at 121 hours on-stream time, with a modified Schulz-Flory probability parameter of 0.39, is plotted against carbon number of synthesis products. The higher heating value of this crude ALKANOL fuel has been calculated to be 70,366 Btu/gal or approximately 60 percent of that of conventional gasoline.

An analysis of the spent catalyst recovered after the 175-hour test showed that it contained 4.1 weight percent carbon and 0.2 weight percent hydrogen. Two effluent liquid samples, which were collected from 0-76 hours on-stream time and from 76-150 hours on-stream, respectively, were analyzed for acid and aldehyde contents. The samples showed values of 0.12 and 0.16 weight percent acid, respectively, with no aldehydes being detected.

3. UCI L-1124 Catalyst (Run 213-82B)

25.0 grams (22.0 cc) of UCI L-1124 calcined catalyst pellets were charged to the Berty reactor and reduced by the same procedure that was used for the activation of UCI L-1122. L-1124 catalyst was tested for 142 hours on-stream time at a constant temperature of about 353°C and pressure of 1500 psig. Two synthesis gases were employed: 2/1 hydrogen/carbon monoxide with 10.8 percent carbon dioxide and 2/1 hydrogen/carbon monoxide with 1.5 percent carbon dioxide. Space velocities ranged from 2150-4650 SL/hr/kg catalyst. Table VI-10 summarizes the run conditions and results for the seven material balance tests made with L-1124 catalyst. Table VI-11 shows the crude ALKANOL fuel distributions for each of the material balance tests made.

CHEM SYSTEMS, INC.

Table VI-10

SUMMARY FOR RUN # 213-82B

TODAY'S DATE : 07/15/81

CATALYST NUMBER : UCI L-1124
ATOMIC FORMULA :
PREP. METHOD : UCI PREP
SURFACE AREA(1) : 0 m^2/gm
BULK DENSITY(1) : 1.14 gm/cc

TEST NUMBER	1	2	3	4	5	6
TEST CONDITIONS :						
FEED H2/CO Ratio	2.17	2.05	2.13	2.13	2.13	2.13
FEED CO2	10.77	10.82	10.99	10.99	10.99	1.64
AVE. TEMP., °C	354.0	353.0	353.0	352.0	354.0	354.0
HOT SPOT, °C	354.0	353.0	353.0	352.0	354.0	354.0
PRESSURE, psig	1520.0	1505.0	1520.0	1520.0	1520.0	1495.0
VHSV, l/hr/kgm cat.	2865.2	2616.2	2771.6	4364.5	2164.3	2637.1
HOURS on STREAM	3.0	96.5	115.0	117.5	119.8	140.5
CONVERSION :						
CO to Prods., vol%	17.25	11.93	10.44	9.49	16.14	12.86
CO to CO2, vol%	5.33	4.27	2.67	0.32	5.87	8.59
CO, gm mol/hr/kgm cat.	6.94	4.64	3.87	4.56	5.07	7.07
STY of Oxygenates(2) gm mol/hr/kgm cat.	3.23	2.15	1.88	2.21	2.17	3.92
STOICHIOM. H2/CO converted	1.49	1.32	1.53	1.84	1.31	1.11
CARBON SELECTIVITY (Normalized Mol % on CO2-free Basis) :						
CH3OH	18.32	17.84	19.89	21.29	18.27	28.41
C2-C6 ALCOHOLS	25.47	25.87	26.68	24.77	22.42	26.38
C2-C6 ALD.&ESTERS	2.78	2.68	2.06	2.33	2.10	0.68
CH4	11.63	11.85	11.41	11.55	14.57	8.81
C2-C3 HYDROCARBONS	15.88	17.87	17.10	17.08	21.99	13.84
C4+ HYDROCARBONS	25.92	23.89	22.85	22.97	20.65	21.87
APPROACH TO(3) WGS Equilibrium, °C :	-15.0	-28.0	-32.6	14.9	-10.3	
CARBON ACCOUNTABILITY,% (4):	123.2	109.4	124.8	99.9	97.8	112.5
OXYGEN REJECTION RATIO,(5):	0.05	0.04	0.04	0.07	0.05	

(1) Fresh, non-reduced catalyst.
(2) Space Time Yield (STY) = VHSV/22.4 * %CO in feed/100 * %CO conv./100 * %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 CO2.

Continued...

CHEM SYSTEMS, INC.

Table VI-10(Concluded)

SUMMARY FOR RUN # 213-82B

TODAY'S DATE : 07/15/81

CATALYST NUMBER : UCI L-1124
ATOMIC FORMULA :
PREP. METHOD : UCI PREP
SURFACE AREA(1) : 0 m^2/gm
BULK DENSITY(1) : 1.14 gm/cc

TEST NUMBER	7

TEST CONDITIONS :

FEED H2/CO Ratio	2.13
FEED CO2	1.64
AVE. TEMP.,°C	354.0
HOT SPOT, °C	354.0
PRESSURE, psig	1500.0
VHSV, l/hr/kgm cat.	4647.3
HOURS on STREAM	141.5

CONVERSION :

CO to Prods., vol%	8.83
CO to CO2, vol%	4.73
CO, gm mol/hr/kgm cat.	7.88
STY of Oxygenates(2) gm mol/hr/kgm cat.	4.41
STOICHIOM. H2/CO converted	1.25

CARBON SELECTIVITY (Normalized Mol % on CO2-free Basis) :

CH3OH	28.04
C2-C6 ALCOHOLS	26.76
C2-C6 ALD.&ESTERS	1.16
CH4	8.50
C2-C3 HYDROCARBONS	12.07
C4+ HYDROCARBONS	23.46

APPROACH TO(3)
WGS Equilibrium, °C :

CARBON ACCOUNTABILITY,% (4): 118.0

OXYGEN REJECTION RATIO,(5):

(1) Fresh, non-reduced catalyst.
(2) Space Time Yield (STY) = VHSV/22.4 * %CO in feed/100 * %CO conv./100 * %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 CO2.

CHEM SYSTEMS INC.

Table VI-11

CRUDE ALKANOL FUEL WI DISTRIBUTION

RUN 213-82

Catalyst Number : UCI L-1124 Date : 6/25/81

Catalyst Formulation: Proprietary Wt% (H_2O FREE)

	TEST #					
COMPONENT	1	2	3	4	5	6
METHANOL	39.101	38.508	41.417	43.796	42.285	51.686
ETHANOL	7.829	11.157	10.626	10.775	13.570	8.454
N-PROP OL	7.004	10.153	10.340	9.317	10.558	10.037
N-BUT OL	5.490	6.679	6.919	7.012	4.213	4.533
N-PENT OL	6.528	3.309	4.033	3.243	3.036	4.043
N-HEX OL	5.787	3.452	2.618	1.611	1.760	2.644
ACET ALD	.384	1.489	1.291	1.506	1.594	.156
PROP ALD	.633	.872	.744	.763	1.001	.615
BUT ALD	2.435	1.218	.660	.758	.497	.000
PENT ALD	.000	.000	.000	.000	.000	.000
HEX ALD	.000	.000	.000	.000	.000	.000
C4 H.C.	5.948	7.198	5.423	6.259	7.104	4.100
C5 H.C.	3.299	4.061	3.828	3.411	4.720	2.799
C6 H.C.	2.439	3.557	3.469	3.395	3.412	2.330
C7 H.C.	7.746	5.829	6.233	6.580	3.968	4.359
C8 H.C.	3.980	1.072	1.463	.900	1.180	2.283
C9 H.C.	1.396	1.444	.939	.674	1.104	1.960
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000
METHANOL	39.101	38.508	41.417	43.796	42.285	51.686
C2 - C6 ALCOHOLS	32.638	34.751	34.535	31.958	33.136	29.712
OTHER C2 - C6 OXYGENATES	3.452	3.580	2.695	3.027	3.091	.770
C4 - C9 HYDROCARBONS	24.809	23.161	21.354	21.219	21.488	17.832
CALCULATED HIGHER HEATING VALUE Btu/gal	90413.	88376.	87365.	86138.	85870.	83910.

Continued...

CHEM SYSTEMS INC.

Table VI-11 (Concluded)

CRUDE ALKANOL FUEL WI DISTRIBUTION

RUN 213-82

Catalyst Number : UCI L-1124 Date : 6/25/81

Catalyst Formulation: Proprietary Wt% (H_2O FREE)

COMPONENT	TEST # 7
METHANOL	49.934
ETHANOL	8.525
N-PROP OL	9.631
N-BUT OL	4.286
N-PENT OL	4.951
N-HEX OL	2.701
ACET ALD	.218
PROP ALD	.672
BUT ALD	.357
PENT ALD	.000
HEX ALD	.000
C4 H.C.	4.127
C5 H.C.	2.740
C6 H.C.	1.992
C7 H.C.	5.130
C8 H.C.	2.830
C9 H.C.	1.906
TOTAL	100.000

METHANOL	49.934
C2 - C6 ALCOHOLS	30.093
OTHER C2 - C6 OXYGENATES	1.248
C4 - C9 HYDROCARBONS	18.725

CALCULATED HIGHER HEATING VALUE
Btu/gal 84835.

FIGURE VI-22

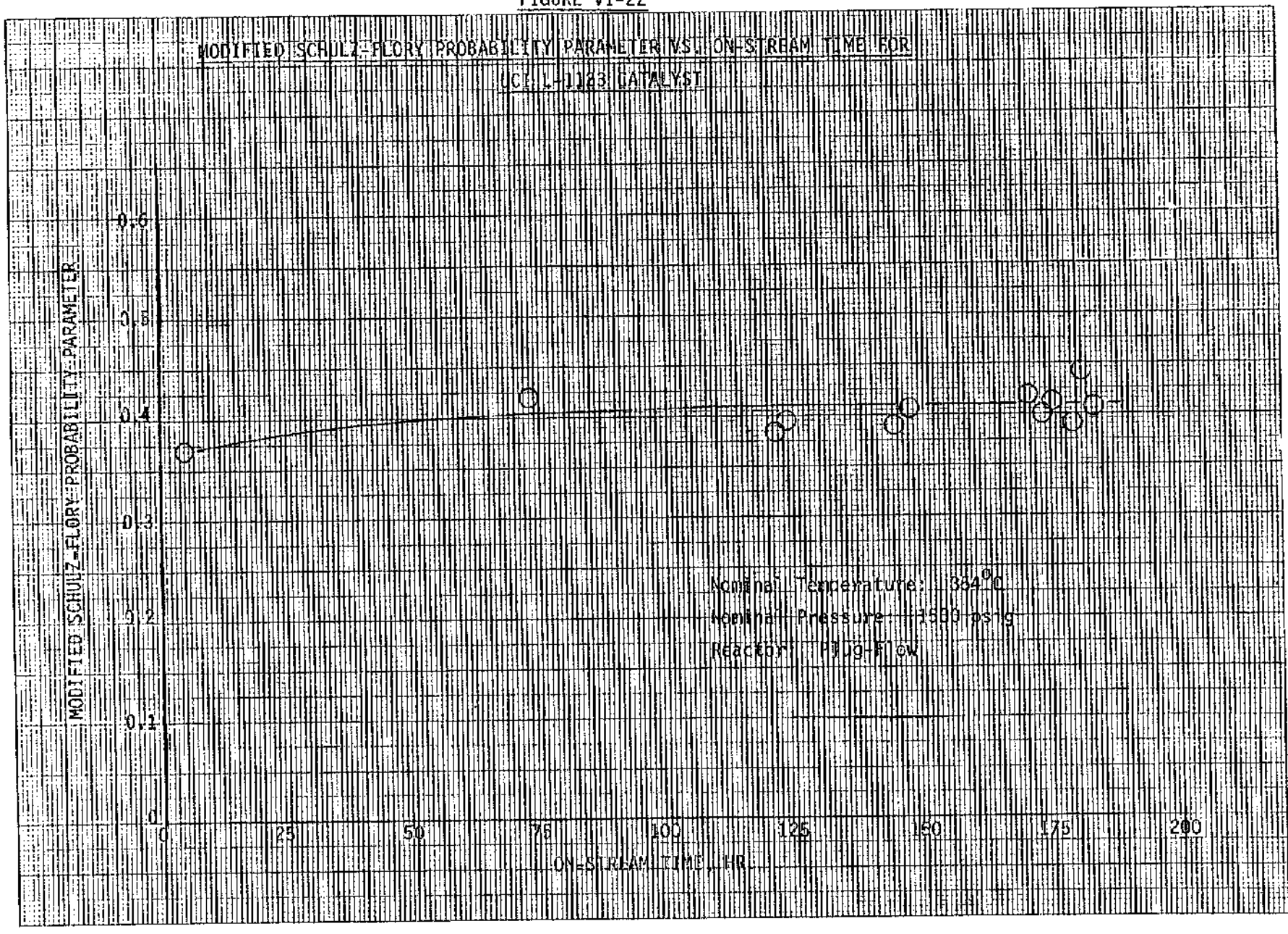
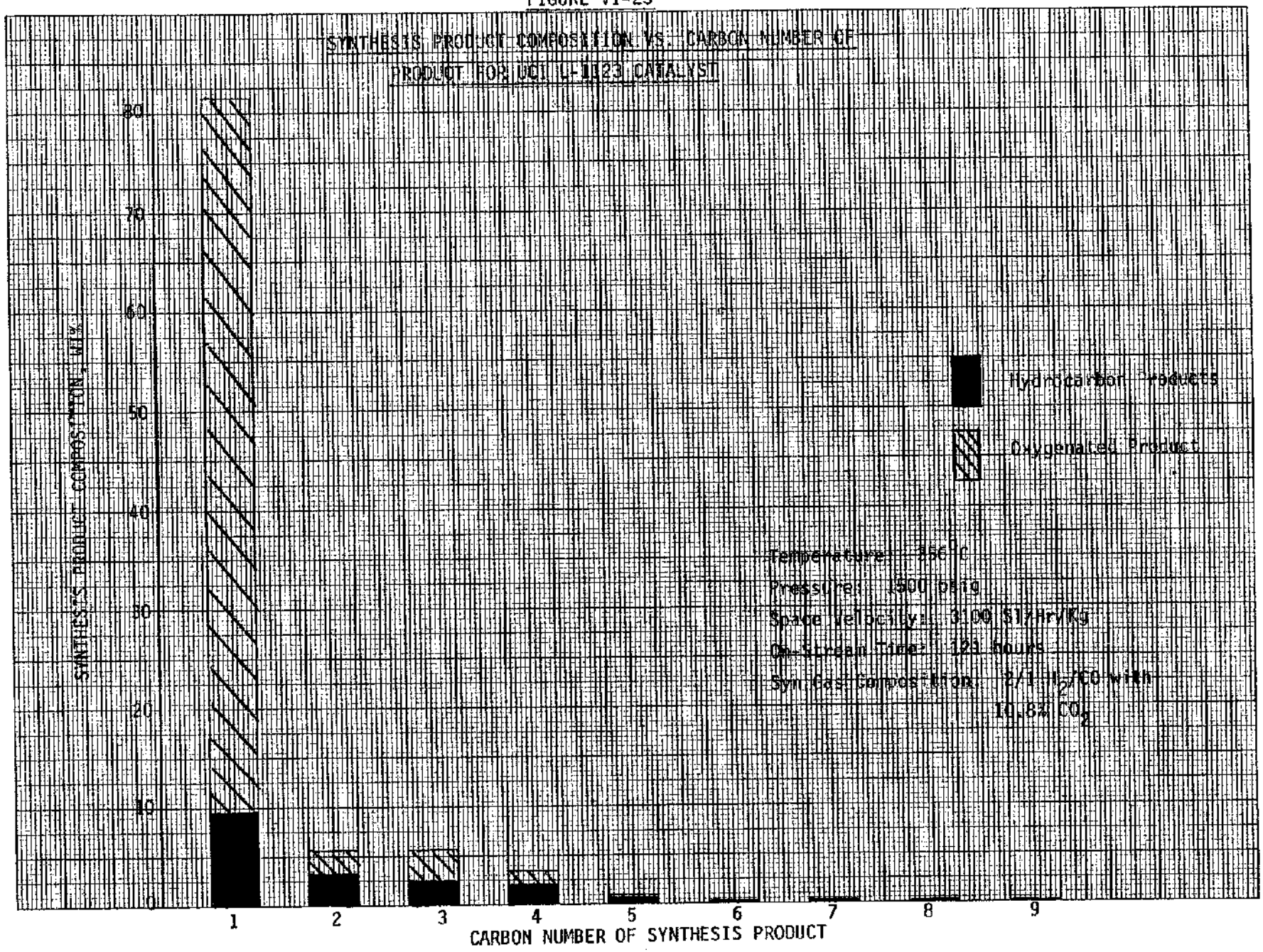

MODIFIED SCHULZ-FLORY PROBABILITY PARAMETER VS. ON-STREAM TIME FOR
UCC L-0183 CATALYST
MODIFIED SCHULZ-FLORY PROBABILITY PARAMETER
0.6
0.4
0.2
0.1
0
0
25
50
75
100
125
150
175
200
ON-STREAM TIME, HR.
Nominal Temperature: 364°C
Nominal Pressure: 1500 psig
Reactor: Plug-Flow

FIGURE VI-23


SYNTHESIS PRODUCT COMPOSITION VS. CARBON NUMBER OF PRODUCT FOR UCI U-1123 CATALYST
SYNTHESIS PRODUCT COMPOSITION, WT %
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
CARBON NUMBER OF SYNTHESIS PRODUCT
Hydrocarbon Products
Oxygenated Products
Temperature: 256°C
Pressure: 1500 psig
Space Velocity: 3100 SL/Hr/Kg
On-Stream Time: 123 hours
Syn Gas Composition: 2/1 H_2/CO with 10.8% CO_2

While data for this catalyst evaluation was very limited, several trends, as depicted in Figure VI-24 through 28, were observed. Figure VI-24 shows that L-1124 catalyst was apparently deactivating over the first 115-hour period maintained at constant space velocity and synthesis gas composition. The lines plotted on the figure at higher on-stream times were based on the assumption that the deactivation at other conditions of space velocity and synthesis gas composition would follow the same trend as observed between 0 and 115 hours on-stream time.

The ALKANOLS selectivity (Figure VI-25) appeared to be unaffected by space velocity. A small effect of carbon dioxide content of the synthesis gas was observed towards the end of the test when the carbon dioxide level was decreased from 10.8 percent to 1.5 percent resulting in an increase in the ALKANOLS selectivity from about 76 percent to 85 percent. The ALKANOLS composition (Figure VI-26) also exhibited a similar trend to that of the ALKANOLS selectivity. However, a more significant effect of carbon dioxide content of the synthesis gas was observed. Synthesis gases containing the higher (10.8%) carbon dioxide content resulted in ALKANOL mixtures having higher concentrations of C_2+ components. However, the higher carbon dioxide levels also resulted in increased light hydrocarbon gas yields as illustrated in the following table:

TABLE VI-12

EFFECT OF CARBON DIOXIDE CONTENT OF 2/1 HYDROGEN/CARBON MONOXIDE SYNTHESIS GASES ON L-1124 CATALYST PERFORMANCE

Carbon Dioxide Level, Percent	1.5	10.8
ALKANOL Selectivity, Weight Percent	85	77
C_1-C_3 H.C. Gas Selectivity, Weight Percent	15	23
Crude ALKANOL Composition, Weight Percent		
Methanol	51	42
C_2-C_6 Oxygenates	31	36
C_4-C_9 Hydrocarbons	18	22
Calculated HHV of ALKANOLS, Btu/Gal	84,375	86,458

FIGURE VI-24

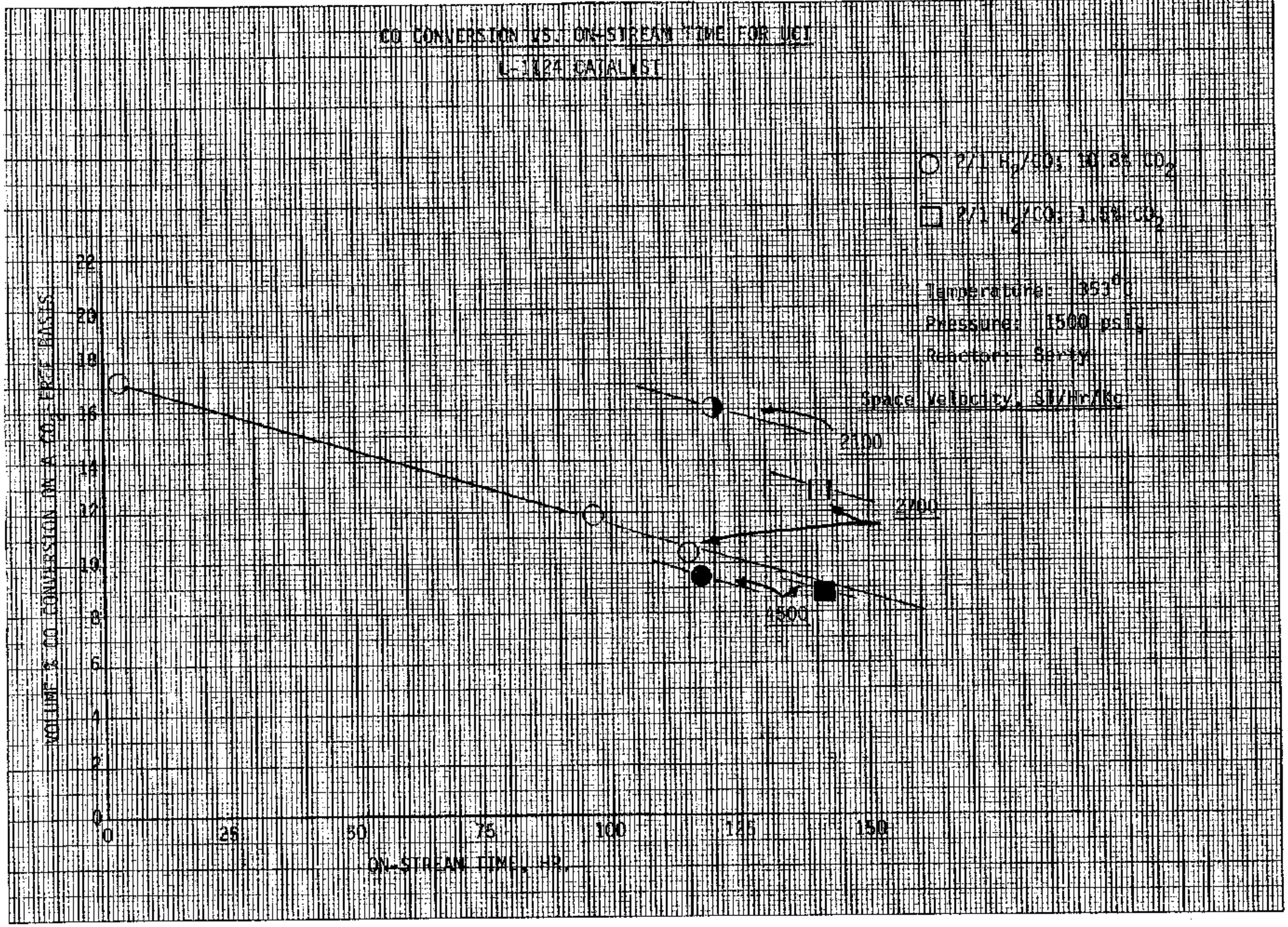

CO CONVERSION VS. ON-STREAM TIME FOR UCI
L-1124 CATALYST
○ 2/1 H_2/CO; 10.8% CO_2
□ 2/1 H_2/CO; 1.5% CO_2
Temperature: 353°C
Pressure: 1500 psig
Reactor: Berty
Space Velocity, Sl/Hr/Kg
2100
2700
4500
VOLUME % CO CONVERSION ON A CO_2 FREE BASIS
0
2
4
6
8
10
12
14
16
18
20
22
0
25
50
75
100
125
150
ON-STREAM TIME, HR.

FIGURE VI-25

ALKANOLS SELECTIVITY VS. ON-STREAM TIME FOR UCI L-1124 CATALYST

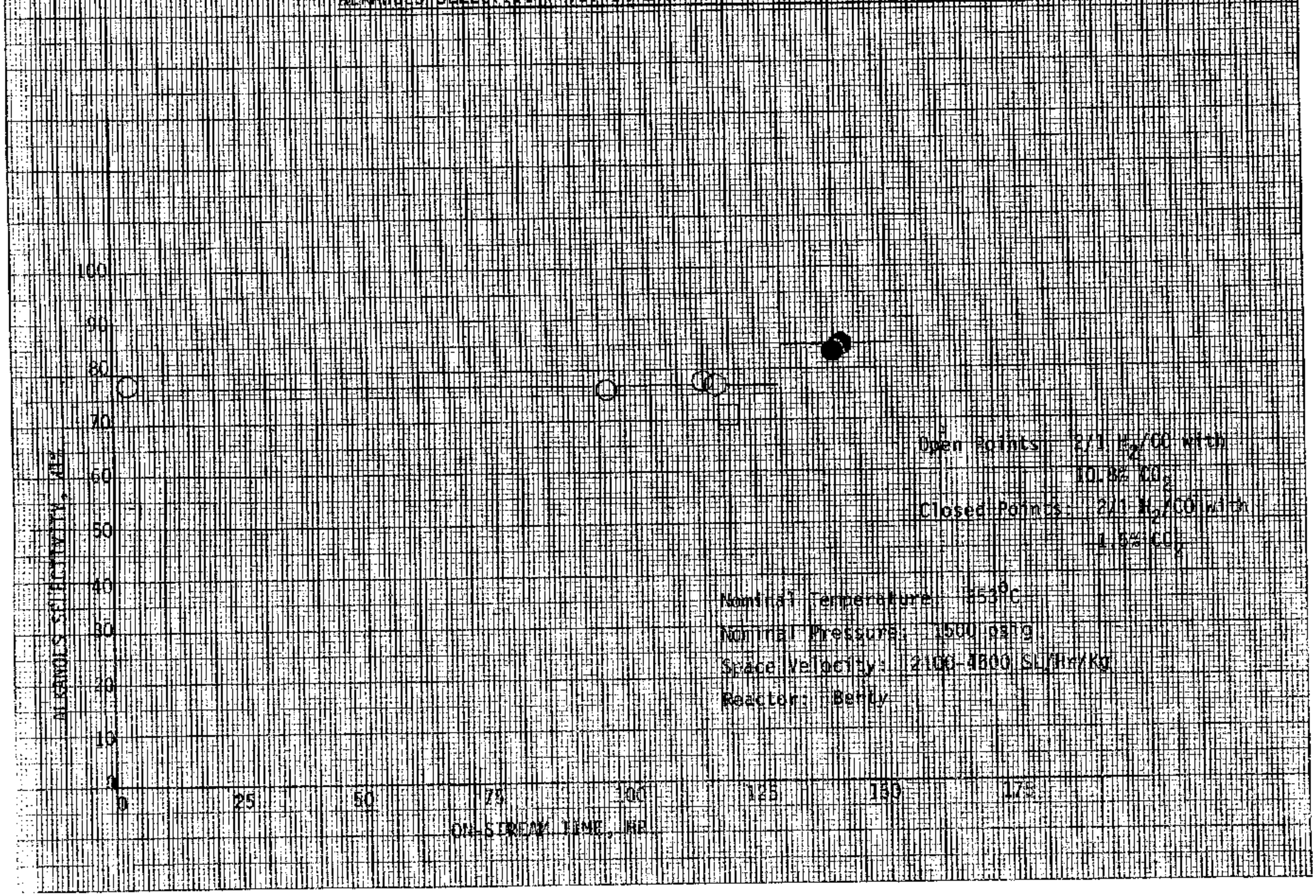
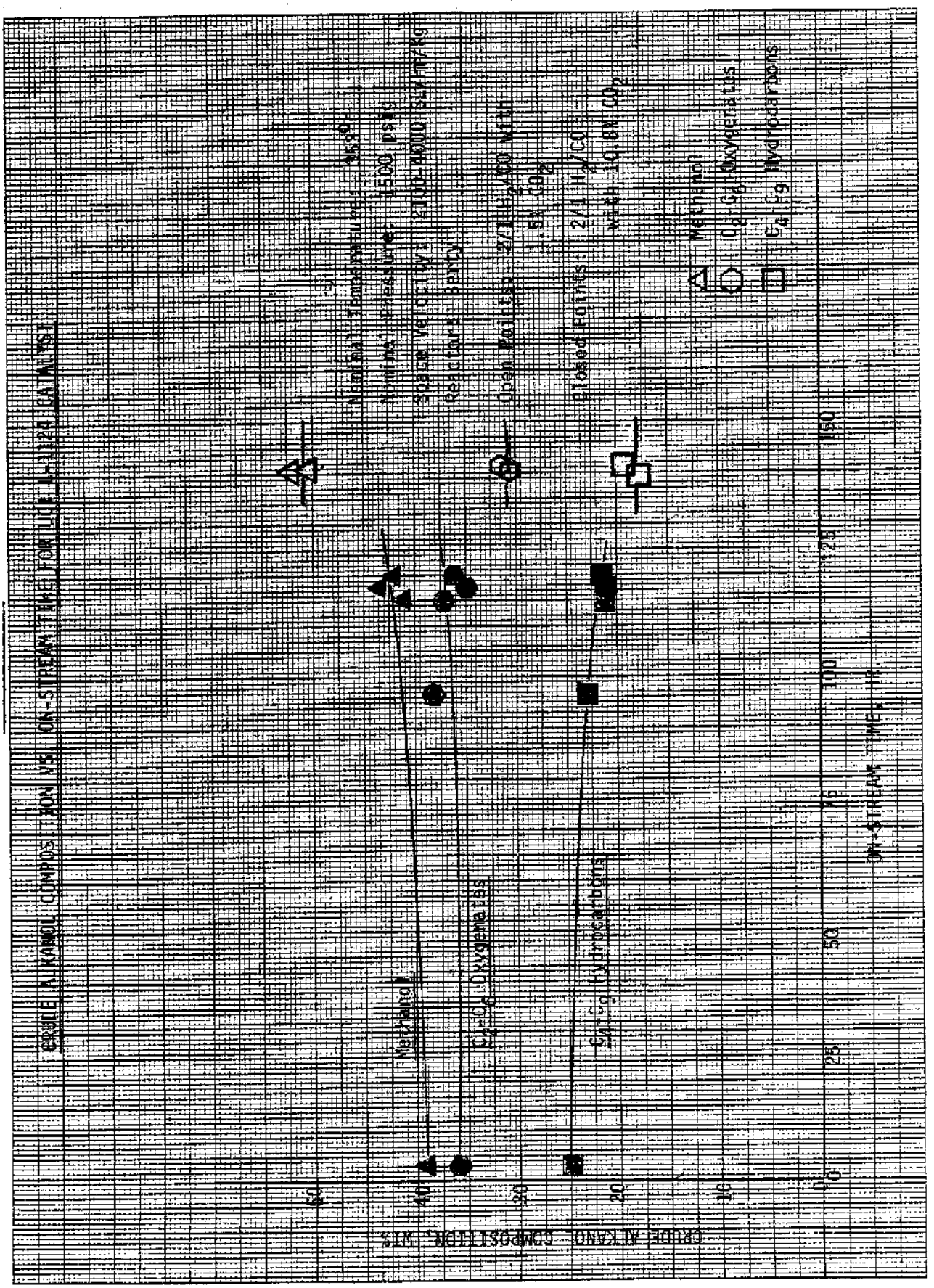


FIGURE VI-26


CRUDE ALCOHOL COMPOSITION VS ON-STREAM TIME FOR LIQUID-PHASE METHANOL
ON-STREAM TIME, HR
CRUDE ALCOHOL COMPOSITION, WT%
Methanol
C2-C5 oxygenates
C1-C5 hydrocarbons
Methanol
C4-C9 oxygenates
C4-C9 hydrocarbons
Nominal temperature: 260°C
Nominal pressure: 1500 psig
Space velocity: 3700-7400 SCF/HR/KG
Recycle ratio: 3:1
Open points: 2/1 H2/CO, 16% CO2
Closed points: 2/1 H2/CO, 10% CO2

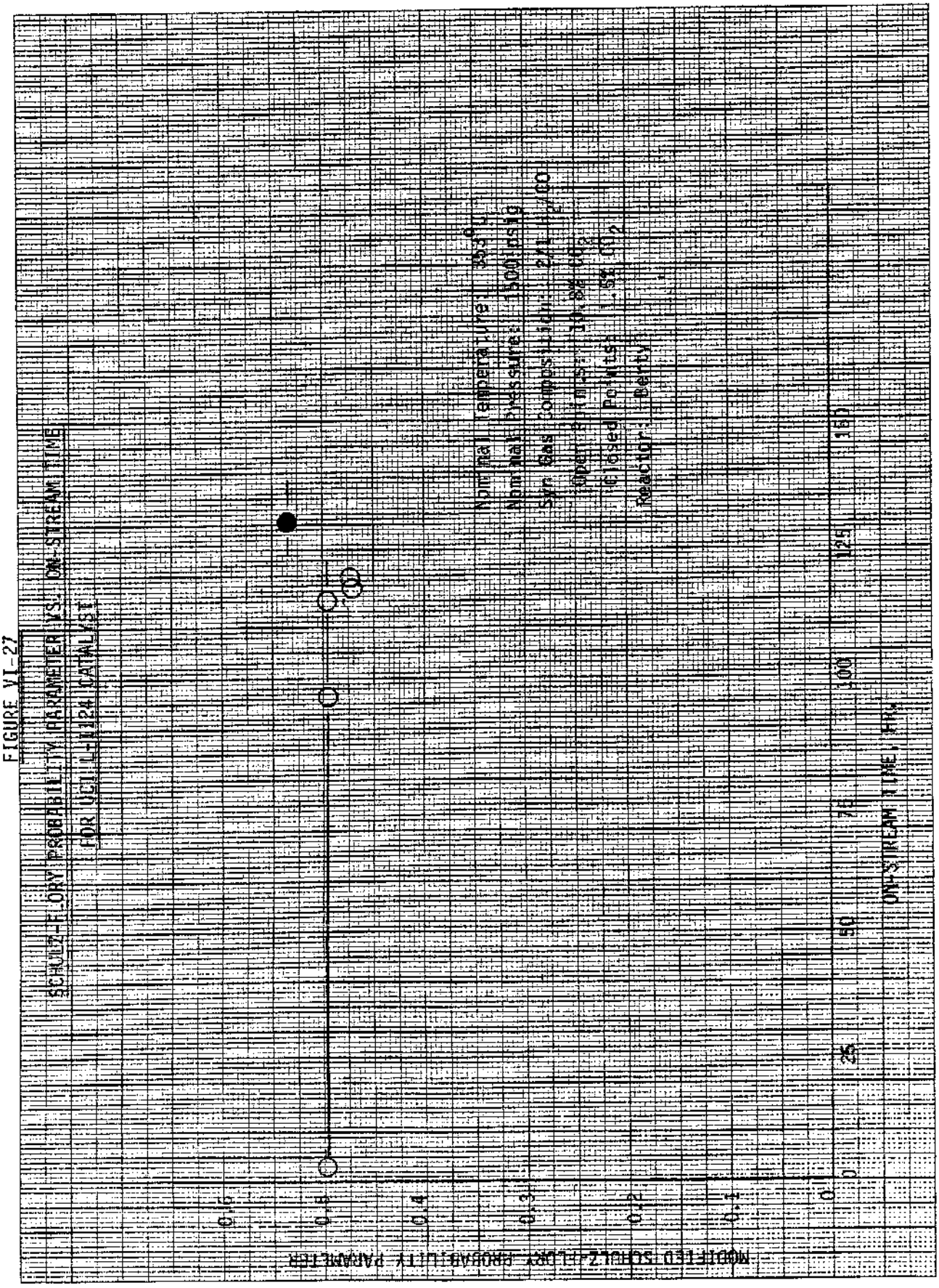
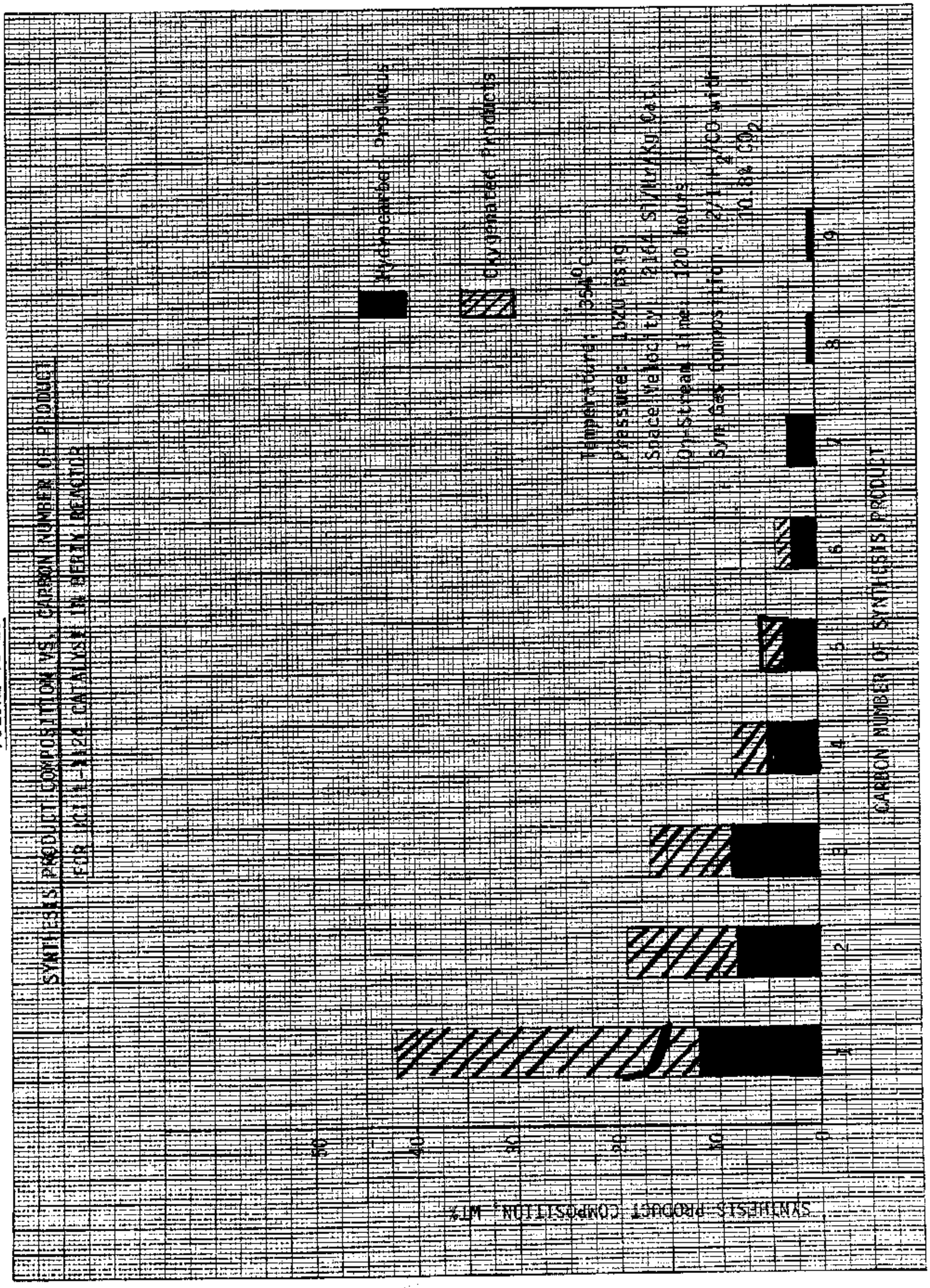


FIGURE VI-27
SCHULZ-FLORY PROBABILITY PARAMETER VS. ON-STREAM TIME
FOR UCI L-1124 CATALYST

FIGURE VI-28


SYNTHESIS PRODUCT COMPOSITION VS. CARBON NUMBER OF PRODUCT
Hydrocarbon Products
Oxygenated Products
Temperature: 354°C
Pressure: 1620 psig
Space Velocity: 2164 Sl/Hr/Kg Cat.
On-Stream Time: 120 hours
Syn Gas Composition: 2/1 H2/CO with 10.8% CO2
SYNTHESIS PRODUCT COMPOSITION, WT%
0
10
20
30
40
50
1
2
3
4
5
6
7
8
9
CARBON NUMBER OF SYNTHESIS PRODUCT

The modified Schulz-Flory distribution dependency on catalyst on-stream time (Figure VI-27) was also influenced by the carbon dioxide content of the synthesis gas. Although there was no significant change in the modified Schulz-Flory probability parameter over the first 115 hours on-stream period, the value of the probability parameter increased by about ten percent after the carbon dioxide content of the synthesis gas was decreased to 1.5 percent at 130 hours on-stream time.

The synthesis product composition as a function of carbon number of synthesis product is shown in Figure VI-28 for a data point obtained at 120 hours on-stream time. The modified Schulz-Flory probability parameter for this data point was calculated to be 0.47.

The spent catalyst recovered at the end of the 141-hour test was analyzed and found to contain 6.3 percent carbon content. The average content of the condensed liquid product collected at the end of the test indicated 0.6 percent acid (as acetic acid) and 0 percent aldehydes.

C. Process Variables Studies In the Slurry-Phase Autoclave Reactor System

Based on the analysis of the results of the process variables studies performed in the vapor-phase reaction systems, UCI catalyst L-1122 was selected for further evaluation in the slurry-phase autoclave reactor system. This catalyst was selected on the basis of better catalyst activity - catalyst age response and on the higher C_2+ alcohol content of the crude ALKANOL mixture. Two test campaigns were performed for L-1122 catalyst using two different catalyst samples. The first test campaign, designated as 226-28S, evaluated the effects of reaction pressure, space velocity, reaction temperature and catalyst age for a constant synthesis gas composition. Twelve material balance tests were made encompassing 558 hours of on-stream time. The slurry vehicle consisted of high purity n-heptadecane.

The second test campaign, designated as 226-42S, was initially formulated to perform a one-month catalyst life test at a fixed set of operating conditions. The life test was abandoned after about 200 hours on-stream

time in favor of further process variables studies. The decision to make this change was based on the low C_2+ oxygenates selectivities observed for the startup conditions of the test.

1. Slurry-Phase Tests With n-Heptadecane Slurry Oil (226-28S)

A sample of UCI L-1122 calcined catalyst was ground using a mortar and pestle, then sieved to 100 percent greater than 70 mesh (210 microns). 100 gms of the resultant powder were charged to a 2-inch diameter vapor-phase, plug-flow reduction reactor. The reduction was carried out at 1 atmosphere pressure using the following procedure:

- Purge reactor with nitrogen while increasing the bed temperature to 200°C.
- Start feeding 2% hydrogen/98% nitrogen reduction gas to the reactor at a rate of 800-900 Sl/hr/kg catalyst. Maintain these conditions for 18 hours.
- Increase the reactor temperature from 200°C to 300°C over a period of 3 hours and hold for 1 hour.
- Increase the reactor temperature from 300°C to 350°C over a period of 3 hours and hold for 22 hours.
- After 22 hours at 350°C, no difference was observed between the concentration of hydrogen in the reduction feed gas and that in the effluent gas. The reduction gas feed was terminated and replaced by nitrogen while the reactor was cooled to room temperature.

Upon cooling, the reactor was pressurized to 25 psig with nitrogen, isolated, and moved to a nitrogen-purged, glove box. In the glove box, the reactor was opened and the reduced catalyst was slurried with 300 ml of n-heptadecane (99 percent purity, Humphrey Chemical Co.) through which nitrogen had been sparged for several hours. The addition of the reduced catalyst increased the volume to 325 ml. The resultant catalyst slurry was charged to the slurry autoclave by the following procedure:

- The autoclave was thoroughly purged with nitrogen and heated to 50°C to prevent freezing of the n-heptadecane.

- 100 ml of nitrogen-purged, n-heptadecane was loaded into the reactor through a port on the head of the autoclave. The nitrogen purge was maintained throughout the entire loading procedure.
- The autoclave impeller was energized with the impeller speed maintained at 600 rpm throughout the rest of the loading procedure.
- The prepared catalyst slurry was then charged to the autoclave through the same port.
- The transfer beaker and all loading lines were washed with an additional 200 ml of n-heptadecane. The reactor was sealed and insulated, and then pressurized with synthesis gas for the start of the run.

The catalyst was evaluated over the total on-stream time of 558 hours utilizing a synthesis gas feed containing 61.5 percent hydrogen, 28.8 percent carbon monoxide, 1.3 percent carbon dioxide and 8.4 percent argon. This gas composition represents that which would satisfy the stoichiometry for total conversion of carbon oxides (carbon monoxide and carbon dioxide) to alcohol products. In practice, the hydrogen content was too low relative to the carbon oxides content for total conversion to alcohol products since the formation of light hydrocarbon gases requires higher hydrogen/carbon monoxide ratios. Table VI-13 contains a summary of the detailed operating conditions and results for the twelve material balance tests made during the run. Table VI-14 contains the crude ALKANOL compositions for each of the material balance periods.

During the run, the oil level in the autoclave was maintained by adding n-heptadecane (using a Milroyal Model DC-1-117R pump) on a daily batchwise basis in an amount equal to the volume of hydrocarbon phase collected in the product separator over the same period. To minimize the oil takeover rate, the reactor was "idled" at 250°C, 1500 psig, 15 SL/hr flow rate, and 600 rpm agitator speed. These times at idle conditions generally occurred overnight, during weekends, and during periods when the analytical system was being calibrated. On-stream time at idle conditions

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Table VI-13

SUMMARY FOR RUN # 226-28S

TODAY'S DATE : 5/14/82

CATALYST NUMBER : UCI L-1122
ATOMIC FORMULA : Proprietary
PREP. METHOD : UCI PREP
SURFACE AREA(1) : m^2/gm
BULK DENSITY(1) : 4.0 gm/cc

TEST NUMBER	1	2	3	4	5	6
TEST CONDITIONS :						
FEED H2/CO Ratio	2.14	2.14	2.14	2.14	2.14	2.14
FEED CO2	1.29	1.29	1.29	1.29	1.29	1.29
AVE. TEMP.,°C	350.0	350.0	350.0	350.0	350.0	325.0
HOT SPOT, °C	350.0	350.0	350.0	350.0	350.0	325.0
PRESSURE, psig	1500.0	1500.0	2500.0	2500.0	2500.0	2500.0
VHSV, l/hr/kgm cat.	1707.6	2503.3	1872.6	3935.4	4238.3	3072.1
HOURS on STREAM	164.9	188.9	260.9	358.7	361.1	383.7
CONVERSION :						
CO to Prods., vol%	20.91	15.23	39.20	48.16	47.97	10.47
CO to CO2, vol%	9.95	8.25	21.76	26.58	25.94	5.04
CO, gm mol/hr/kgm cat.	6.78	7.56	14.68	37.81	40.28	6.13
STY of Oxygenates(2) gm mol/hr/kgm cat.	4.03	4.45	5.66	12.79	13.07	2.34
STOICHIOM. H2/CO converted	1.19	1.15	0.99	1.13	1.11	1.19
CARBON SELECTIVITY (Normalized Mol % on CO2-free Basis) :						
CH3OH	30.24	29.00	7.69	4.73	4.72	5.61
C2-C6 ALCOHOLS	21.55	22.90	23.73	23.00	21.45	25.83
C2-C6 ALD.&ESTERS	7.61	6.90	7.15	6.01	6.28	6.67
CH4	8.85	9.87	11.06	13.41	13.61	15.44
C2-C3 HYDROCARBONS	11.44	12.74	14.91	18.91	16.45	16.62
C4+ HYDROCARBONS	20.30	18.51	35.45	33.85	37.49	29.83
APPROACH TO(3) WGS Equilibrium, °C :	5.0	-63.6	38.4	14.9	27.8	126.1
CARBON ACCOUNTABILITY,% (4):	98.0	99.9	98.1	104.0	103.0	99.7
OXYGEN REJECTION RATIO,(5):	0.07	0.03	0.15	0.16	0.18	0.17

(1) Fresh, non-reduced catalyst.
(2) Space Time Yield (STY) = VHSV/22.4 * %CO in feed/100 * %CO conv./100 * %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 CO2.

Continued...

CHEM SYSTEMS, INC.

Table VI-13 (Concluded)

SUMMARY FOR RUN # 226-28 S

TODAY'S DATE : 5/23/82

CATALYST NUMBER : UCI L-1122
ATOMIC FORMULA : Proprietary
PREP. METHOD : UCI PREP
SURFACE AREA(1) : m^2/gm
BULK DENSITY(1) : 4.0 gm/cc

TEST NUMBER	7	8	9	10	11	12
TEST CONDITIONS :						
FEED H2/CO Ratio	2.14	2.14	2.14	2.14	2.14	2.14
FEED CO2	1.29	1.29	1.29	1.29	1.29	1.29
AVE. TEMP., °C	350.0	350.0	350.0	350.0	245.0	350.0
HOT SPOT, °C	350.0	350.0	350.0	350.0	245.0	350.0
PRESSURE, psig	1500.0	2000.0	1950.0	2500.0	1500.0	1500.0
VHSV, l/hr/kgm cat.	1446.5	2503.4	1611.9	5567.6	417.8	2772.9
HOURS on STREAM	435.6	484.7	486.9	509.7	552.1	558.4
CONVERSION :						
CO to Prods., vol%	18.50	15.68	19.26	8.83	1.79	17.95
CO to CO2, vol%	11.03	8.09	10.20	4.14	0.42	9.63
CO, gm mol/hr/kgm cat.	5.49	7.65	6.11	9.28	0.12	9.83
STY of Oxygenates(2) gm mol/hr/kgm cat.	1.69	2.62	1.98	2.86	0.02	3.27
STOICHIOM. H2/CO converted	1.01	1.36	1.33	1.41	1.69	1.29
CARBON SELECTIVITY (Normalized Mol % on CO2-free Basis) :						
CH3OH	5.48	5.30	5.82	6.10	2.93	4.28
C2-C6 ALCOHOLS	22.05	21.35	20.36	18.79	9.22	22.32
C2-C6 ALD.&ESTERS	3.16	7.66	6.26	5.92	8.20	6.62
CH4	16.06	26.90	28.04	29.85	55.05	25.27
C2-C3 HYDROCARBONS	31.44	20.58	21.86	20.99	14.64	20.99
C4+ HYDROCARBONS	21.81	18.21	17.66	18.35	9.96	20.53
APPROACH TO(3) WGS Equilibrium, °C :	66.3	95.9	93.4	106.2	183.5	91.1
CARBON ACCOUNTABILITY,% (4):	93.2	103.1	98.6	99.9	71.3	102.3
OXYGEN REJECTION RATIO,(5):	0.14	0.18	0.18	0.18	0.13	0.17

(1) Fresh, non-reduced catalyst.
(2) Space Time Yield (STY) = VHSV/22.4 * %CO in feed/100 * %CO conv./100 * %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 CO2.

CHEM SYSTEMS INC.

Table VI-14

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 226-28 S

Catalyst Number : UCI L-1122 Date : 11/9/81

Catalyst Formulation: Proprietary (UCI Catalyst) Wt% (H_2O FREE)

	TEST #					
COMPONENT	1	2	3	4	5	6
METHANOL	52.721	51.499	18.089	12.581	12.189	13.992
ETHANOL	9.335	12.207	14.459	16.087	8.540	24.670
N-PROP OL	7.460	7.244	8.567	5.925	5.791	7.972
N-BUT OL	2.434	2.781	4.472	3.984	4.132	5.006
N-PENT OL	3.035	3.207	6.132	6.077	5.988	2.976
N-HEX OL	1.554	1.162	1.640	6.135	8.600	1.725
ACET ALD	.000	.000	.515	.833	.814	3.827
PROP ALD	2.419	2.973	1.668	1.809	3.024	3.503
BUT ALD	3.985	3.280	1.930	1.524	1.677	2.957
PENT ALD	1.173	.882	.880	.000	.000	.000
HEX ALD	.000	.000	4.288	4.715	3.661	.000
C4 H.C.	3.536	3.831	6.670	7.709	7.786	7.706
C5 H.C.	4.331	3.608	7.438	7.993	8.041	6.958
C6 H.C.	2.276	2.841	7.083	6.673	9.509	6.648
C7 H.C.	2.888	2.620	10.282	7.054	7.803	5.798
C8 H.C.	1.006	1.428	.833	7.195	8.137	4.406
C9 H.C.	1.848	.437	5.053	3.707	4.308	1.855
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000
METHANOL	52.721	51.499	18.089	12.581	12.189	13.992
C2 - C6 ALCOHOLS	23.818	26.601	35.270	38.208	33.051	42.349
OTHER C2 - C6 OXYGENATES	7.577	7.134	9.281	8.881	9.176	10.287
C4 - C9 HYDROCARBONS	15.885	14.765	37.360	40.330	45.583	33.372
CALCULATED HIGHER HEATING VALUE Btu/gal	82585.	82172.	98282.	100951.	103132.	95472.

Continued...

CHEM SYSTEMS INC.

Table VI-14 (Concluded)

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 226-28 S

Catalyst Number : UCI L-1122 Date : 11/9/81

Catalyst Formulation: Proprietary (UCI Catalyst) Wt% (H_2O FREE)

	TEST #					
COMPONENT	7	8	9	10	11	12
METHANOL	17.129	16.664	18.916	20.149	15.705	13.495
ETHANOL	29.002	22.924	24.179	22.430	15.803	22.309
N-PROP OL	8.945	8.287	8.548	8.063	8.834	8.078
N-BUT OL	5.450	4.143	4.362	5.398	7.263	6.121
N-PENT OL	2.687	2.628	2.594	.676	.432	2.712
N-HEX OL	.000	5.331	3.507	3.916	.000	5.791
ACET ALD	1.502	2.217	1.873	4.054	10.797	1.784
PROP ALD	3.542	5.088	4.559	6.903	17.079	5.268
BUT ALD	1.035	6.988	5.659	.553	.000	5.372
PENT ALD	.000	.000	.000	.660	.000	.000
HEX ALD	.000	.000	.000	.000	.000	.000
C4 H.C.	10.522	8.336	8.927	8.685	11.386	8.561
C5 H.C.	9.570	6.182	6.131	5.805	10.601	6.073
C6 H.C.	6.642	4.013	4.225	2.641	.422	4.464
C7 H.C.	2.335	3.453	4.421	3.071	.491	4.866
C8 H.C.	1.638	2.553	1.680	3.064	.559	4.068
C9 H.C.	.000	1.195	.419	3.932	.628	1.038
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000
METHANOL	17.129	16.664	18.916	20.149	15.705	13.495
C2 - C6 ALCOHOLS	46.084	43.313	43.190	40.482	32.332	45.011
OTHER C2 - C6 OXYGENATES	6.078	14.293	12.091	12.171	27.876	12.425
C4 - C9 HYDROCARBONS	30.708	25.731	25.803	27.198	24.087	29.070
CALCULATED HIGHER HEATING VALUE Btu/gal	92648.	93951.	92726.	92399.	90165.	96051.

is included in all on-stream times reported in the computerized run summaries. The catalyst performance at a typical idle condition is shown in Test #11 (552 hours on-stream) on Table VI-13.

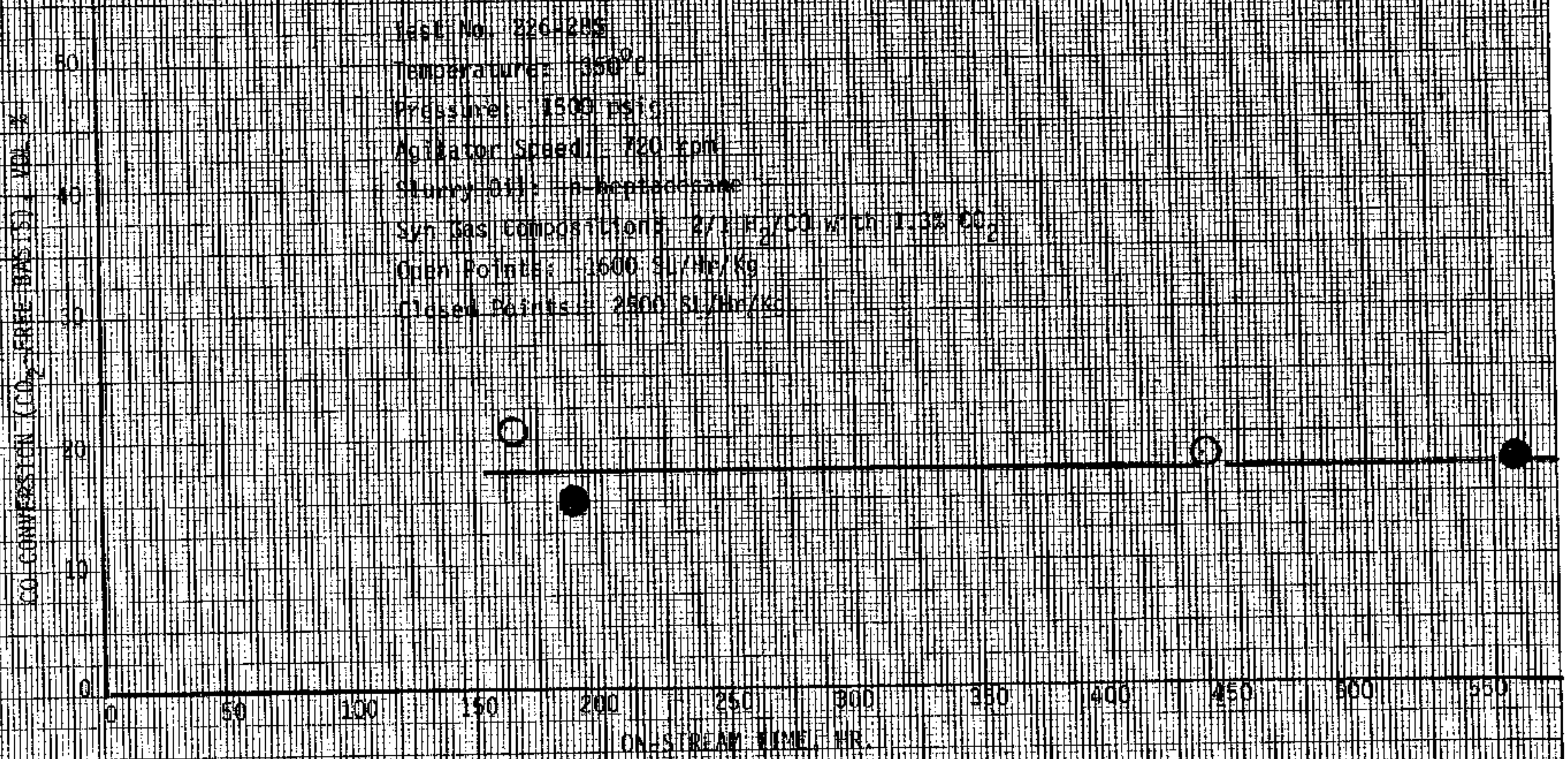
During the first 390 hours on-stream time, vibrational problems were experienced with the agitator. At approximately 390 hours on-stream, the vibrations abruptly ceased. During the disassembly of the reactor upon the conclusion of the run, it was discovered that the agitator assembly had failed and was irreparably damaged. It seems likely that this failure occurred at the time that the vibrations from the agitator ceased. However, there were no clearcut confirmations that this problem indeed occurred as evidenced from the data analysis. In any event, a trend analysis of the observed data was performed assuming that there was no significant impact of the degree of agitation on the catalyst performance.

Figure VI-29 shows the effect of on-stream time on carbon monoxide conversion at 1500 psig reaction pressure. No data were taken during the initial 150 hours on-stream time in order to allow the catalyst to undergo a period of stabilization. It appears that over the latter 400 hours on-stream time, there was no catalyst deactivation with respect to carbon monoxide conversion.

The apparent effect of space velocity on carbon monoxide conversion is depicted in Figure VI-30. As can be seen from the figure, there appears to be an unusual maxima in the space velocity - carbon monoxide conversion relationship. As space velocity was decreased from 5500 to 4000 SL/hr/kg, the carbon monoxide conversion level increased as would be expected. However, further decreases in space velocity to the 2000 SL/hr/kg level did not result in corresponding increases in the conversion level. In fact, the carbon monoxide conversion decreased about 15 percent (relative) upon decreasing space velocity from the 4000 to the 2000 SL/hr/kg level. The data points shown on the figure do span a catalyst on-stream time of from 261 to 510 hours and any possible time-dependent effects such as the agitator problem (occurred at 390 hours on-stream time) could be clouding the interpetation of the data. Another point of interest is that the carbon monoxide conversion to carbon dioxide via water-gas shift at the

FIGURE VI-29

EFFECT OF ON-STREAM TIME ON CO CONVERSION FOR UCI L-1122 CATALYST IN SLURRY-PHASE AUTOCLAVE REACTION SYSTEM



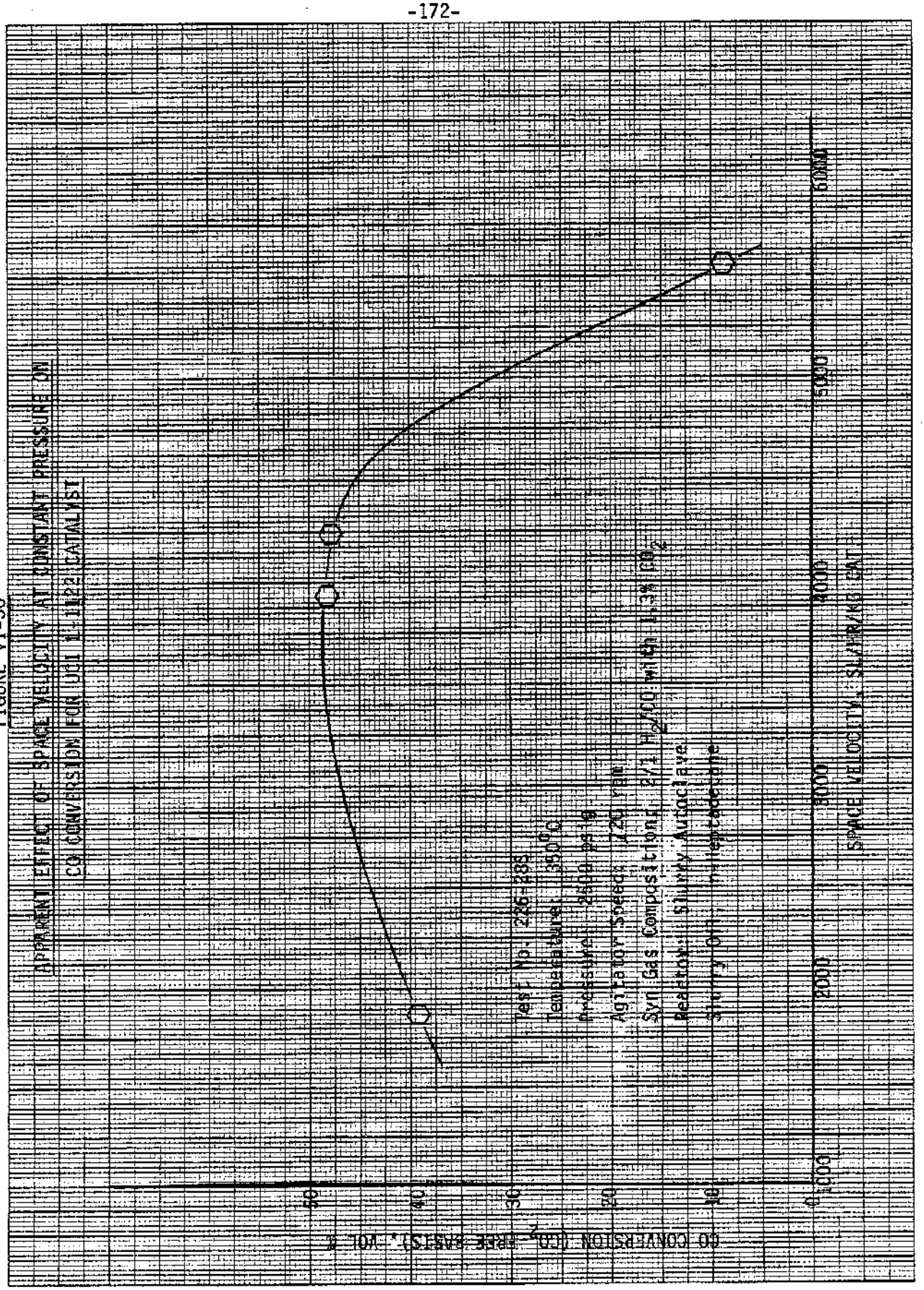

APPARENT EFFECT OF SPACE VELOCITY AT CONSTANT PRESSURE ON
CO CONVERSION FOR UCI 1-1122 CATALYST
Pressure: 226 PSIG
Temperature: 250°C
Agitator Speed: 1720 RPM
Syngas Composition: 2/1 H2/CO with 1.3% CO2
Reactor: Slurry Autoclave
Slurry Oil: Hydrocracked
CO CONVERSION (CO2 FREE BASIS), VOL %
SPACE VELOCITY, SL/HR/KG CAT

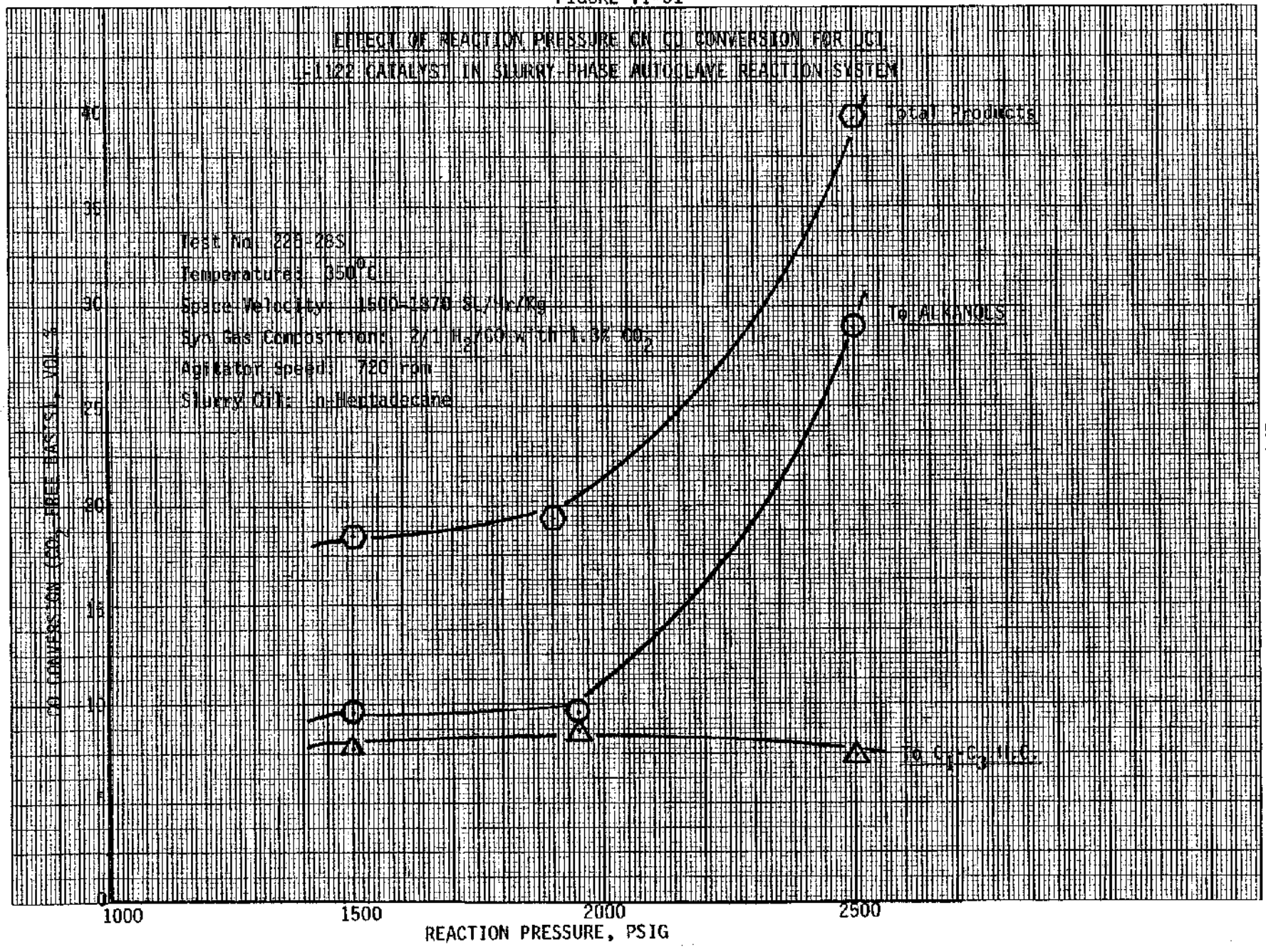
FIGURE VI-30

5500 space velocity level was only about 4 percent as compared to 21-27 percent at the 2000-4000 space velocity level. This is equivalent to about an 85 percent (relative) decrease in carbon monoxide conversion which is approximately the same as the relative decrease observed for the carbon monoxide conversion to alcohols and hydrocarbons.

The effect of reaction pressure on carbon monoxide conversion is shown in Figure VI-31. The relatively large increase in activity upon increasing reactor pressure from the 2000 to the 2500 psig level is attributable to increased ALKANOLS yields, and in particular, the C_4-C_9 hydrocarbon component of the ALKANOLS.

There appeared to be essentially little or no effect of the reaction conditions, i.e., space velocity, pressure, etc., on the selectivity to and composition of the crude ALKANOLS. These catalyst performance parameters appeared to be entirely controlled by the catalyst age as measured by on-stream time. This phenomenon is qualitatively similar to that observed with L-1122 catalyst in the Berty vapor-phase reactor and is illustrated in Figures VI-32, 33, 34 and 35, which show the effects of on-stream time on ALKANOLS selectivity, methanol content, C_2-C_6 oxygenates content and C_4-C_9 hydrocarbon content of ALKANOLS, respectively. As can be seen from the figures, it appears that by the end of the 550-hour test, the selectivity and composition of the ALKANOLS leveled off at relatively constant values. The directional changes in methanol content of ALKANOLS paralleled those observed in the Berty reactor for L-1122 catalyst. In the slurry autoclave test, the C_4-C_9 hydrocarbon content of the ALKANOLS appears to pass through a maximum point equivalent to 40 percent at about 300-350 hours on-stream time prior to leveling off at 25 percent. In the Berty reactor, the C_4-C_9 hydrocarbon content approached its maximum of about 25 percent asymptotically and did not pass through a maximum point. The C_2-C_6 oxygenates content in the slurry autoclave tests also approached its maximum of about 57 percent asymptotically. In the case of the Berty reactor, C_2-C_6 oxygenates passed through a maximum point equivalent to about 50 percent at 400-450 hours on-stream time prior to leveling off at 42 percent.

FIGURE VI-31


EFFECT OF REACTION PRESSURE ON CO CONVERSION FOR LCL
L-1122 CATALYST IN SLURRY PHASE AUTOCLAVE REACTION SYSTEM
Total Products
To ALKANOLS
To C_1-C_3 H.C.
Test No. 228-28S
Temperature: 250°C
Space Velocity: 1500-1970 SL/Hr/Kg
Syn Gas Composition: 2/1 H_2/CO with 1.3% CO_2
Agitator Speed: 720 rpm
Slurry Oil: n-Heptadecane
CO CONVERSION (CO_2 FREE BASIS), VOL %
0
5
10
15
20
25
30
35
40
1000
1500
2000
2500
REACTION PRESSURE, PSIG

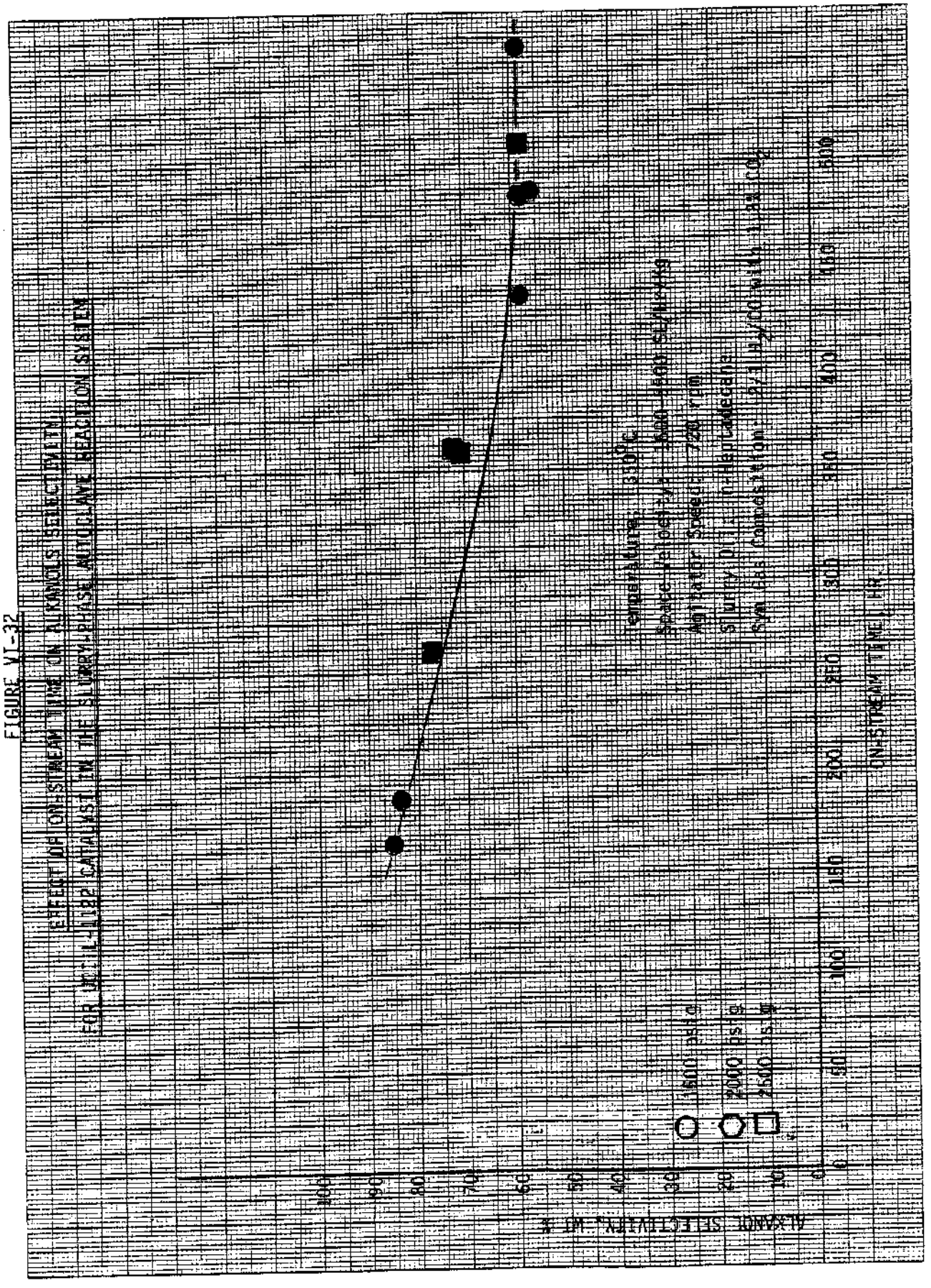


FIGURE VI-32

EFFECT OF ON-STREAM TIME ON ALKANOLS SELECTIVITY FOR THE LIQUID CATALYST IN THE SLURRY-PHASE MITSUBISHI REACTION SYSTEM

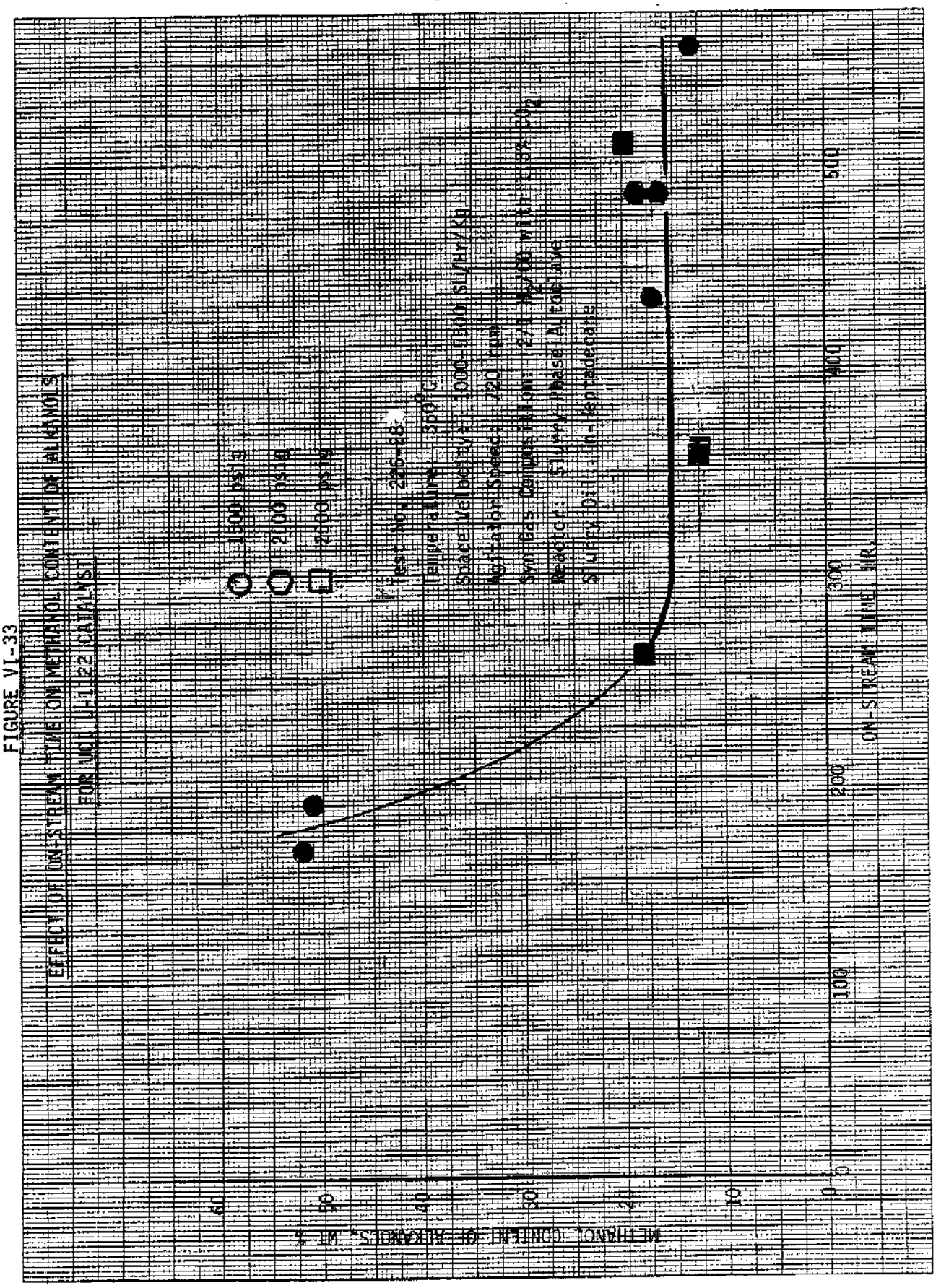
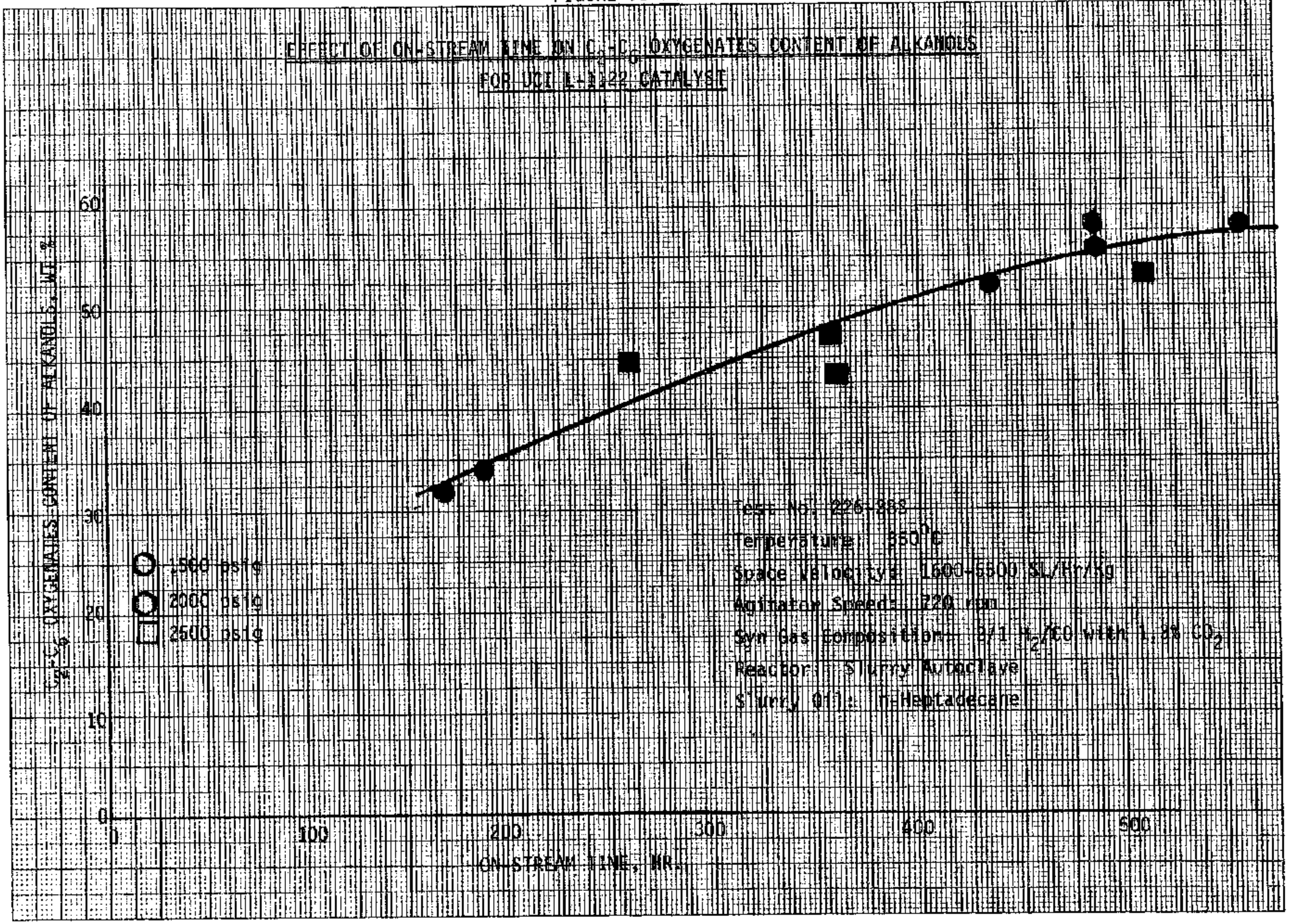


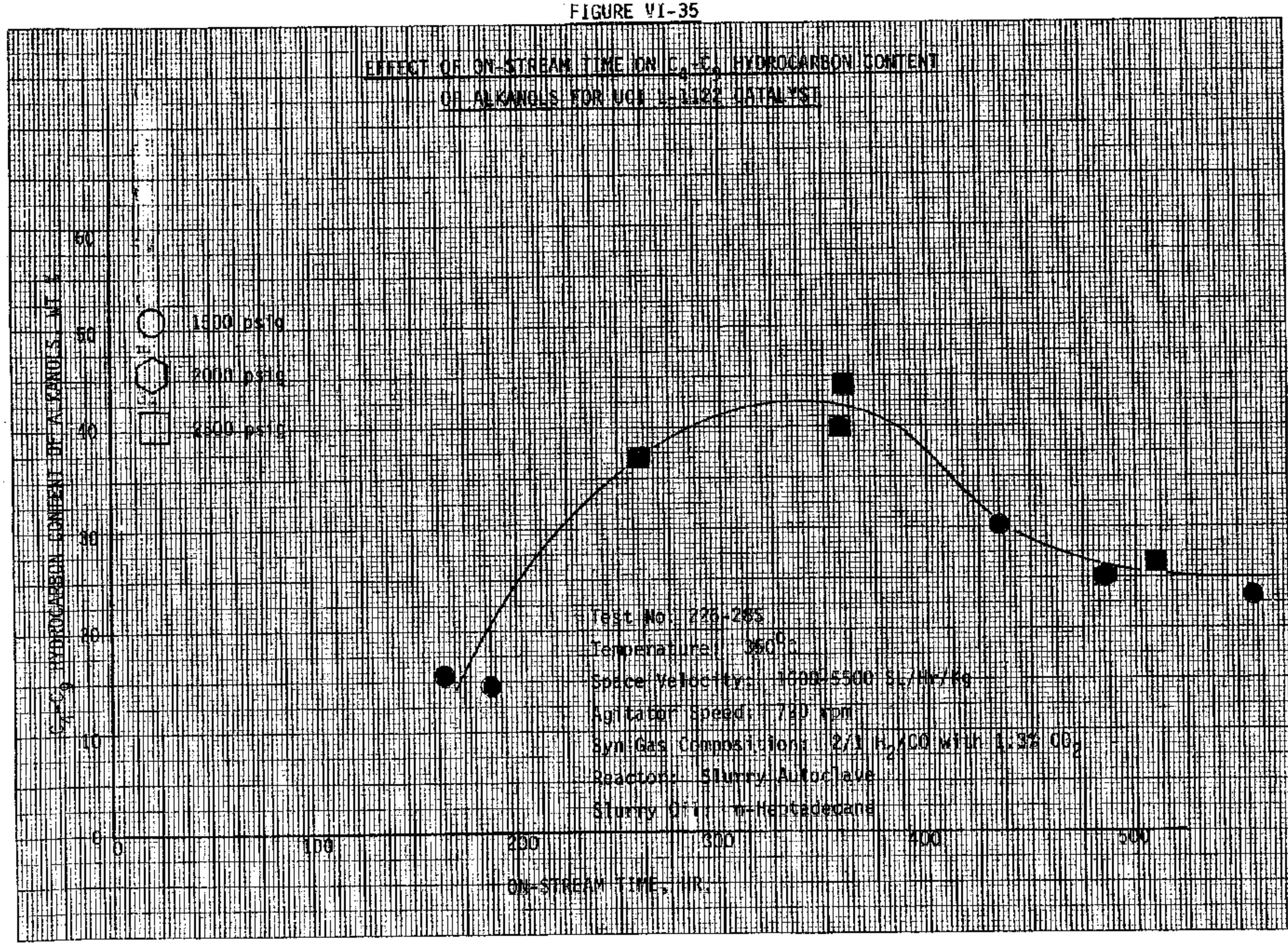
FIGURE VI-33
EFFECT OF ON-STREAM TIME ON METHANOL CONTENT OF ALKANOLS FOR UCC FT-2 CATALYST

FIGURE VI-34



EFFECT OF ON-STREAM TIME ON C_2-C_6 OXYGENATES CONTENT OF ALKANOLS FOR UCI L-1122 CATALYST

FIGURE VI-35


EFFECT OF ON-STREAM TIME ON C_4-C_9 HYDROCARBON CONTENT
OF ALKANOLS FOR UCI 1-1122 CATALYST
1500 psig
2000 psig
2500 psig
Test No. 226-285
Temperature: 360°C
Space Velocity: 1000-5500 SL/Hr/Kg
Agitator Speed: 750 rpm
Syn Gas Composition: 2/1 H_2/CO with 1.3% CO_2
Reactor: Slurry Autoclave
Slurry Oil: n-Heptadecane
C_4-C_9 HYDROCARBON CONTENT OF ALKANOLS, WT %
ON-STREAM TIME, HR.
0
10
20
30
40
50
60
100
200
300
400
500