

A modified Schulz-Flory analysis was applied to the slurry autoclave data for L-1122 catalyst as shown in Figure VI-36. The modified Schulz-Flory probability parameter appeared to pass through a maximum point of about 0.65 at 250-300 hours on-stream time prior to levelling off at a value of 0.50. This is a very similar trend to that observed for L-1122 catalyst evaluated in the Berty reactor. The carbon number distribution at 558 hours on-stream time in the slurry autoclave is shown in Figure VI-37. The modified Schulz-Flory probability parameter at this time was 0.50. Although the carbon number distribution for L-1122 catalyst was essentially equivalent in both the slurry-phase and Berty vapor-phase reactors, there were noticeable differences in the hydrocarbon/oxygenates ratios. This can be clearly seen in Figure VI-37 by comparing the relative areas of the darkened regions (hydrocarbons) to those of cross-hatched regions (oxygenates) for a given carbon number. Most obvious is the C_1 product split, namely, methane and methanol. The methane/methanol weight ratio was about 2.7 as compared to about 0.5 for data obtained in the Berty reactor. The high methane yields might be somewhat attributable to possible hydrocracking of n-heptadecane, the slurry oil, by the ALKANOLS synthesis catalyst. An ensuing test (226-42S) in the slurry autoclave was made with a wider boiling range mineral oil characterized by paraffinic and naphthenic stocks. The resultant methane/methanol weight ratios in this test were lower than that of the slurry test utilizing n-heptadecane and even lower than that of the Berty vapor-phase reactor test.

2. Slurry-Phase Tests With Witco 40 Mineral Oil (226-42S)

The entire head assembly of the slurry autoclave reactor, which had suffered damage during test 226-28S, was replaced with a head assembly from another autoclave reactor. This enabled the continuation of testing with a minimum of lost time. One hundred grams of -70 mesh UCI L-1122 calcined catalyst were reduced and slurried with 600 ml of Witco-40, a white paraffinic mineral oil. The properties of this oil are shown in Table VI-15. With the exception of the slurry oil employed, the reduction and transfer procedures used during this run were identical to those used during test 226-28S. Make-up oil was added continuously using an Altex

TABLE VI-15

PHYSICAL PROPERTIES OF WITCO 40 MINERAL OIL

Hydrocarbon Type:	72% Paraffinic, 20% Naphthenic	
Carbon Number Distribution:	C ₁₄	5%
	C ₁₄ -C ₁₅	15%
	C ₁₆ -C ₁₇	20%
	C ₁₈ -C ₁₉	25%
	C ₂₀ -C ₂₁	20%
	C ₂₁	15%
API Gravity - 60/60°F:	43.2	
Viscosity at 100°F	cp	3.4
	SUS	40
Distillation (ASTM D86), °F	IBP	518
	5% Distilled	528
	10	540
	50	568
	90	634
	95	657
	EP	659
	Sulfur (ASTM D1266), ppm	1

FIGURE VI-36

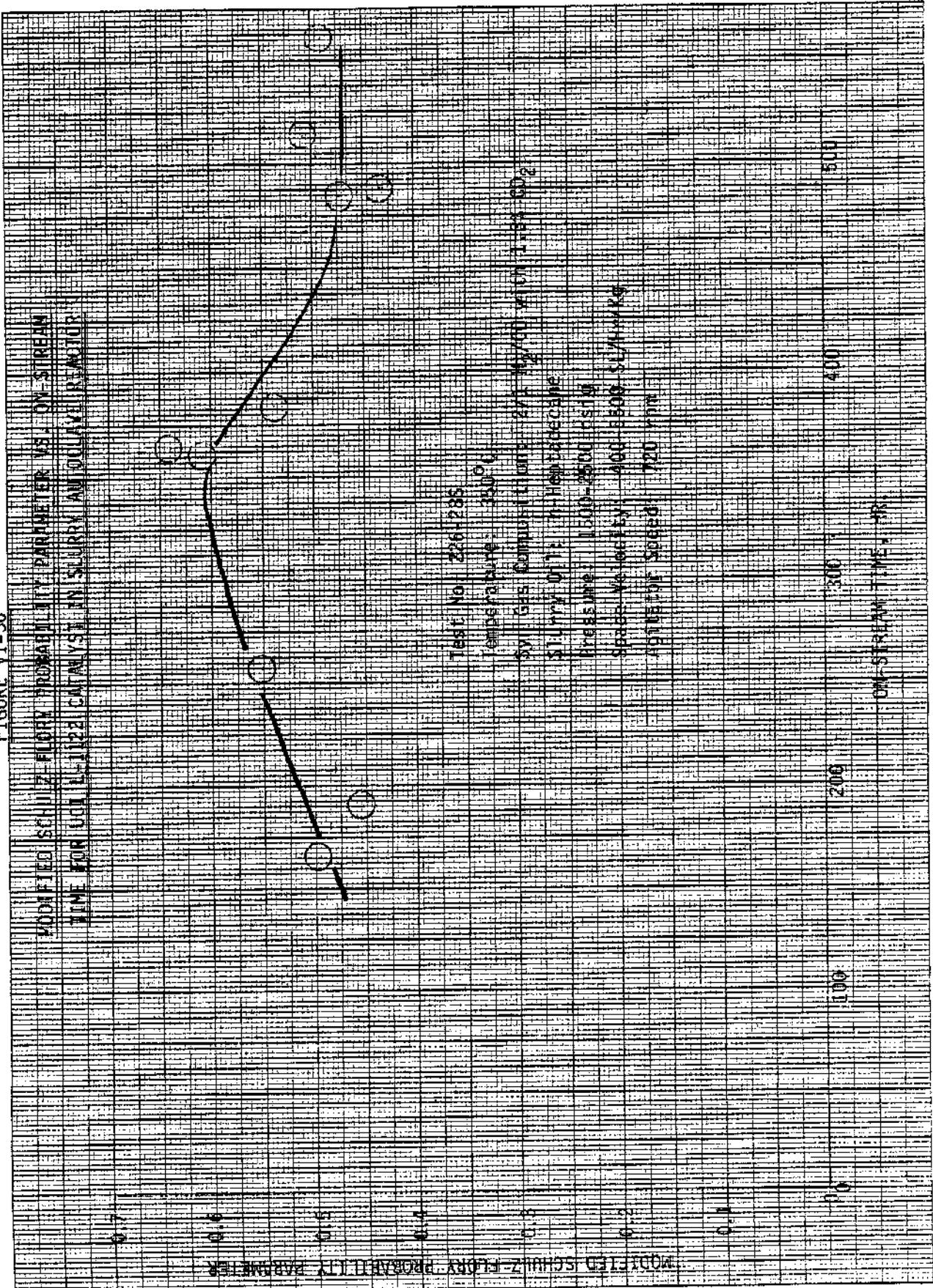
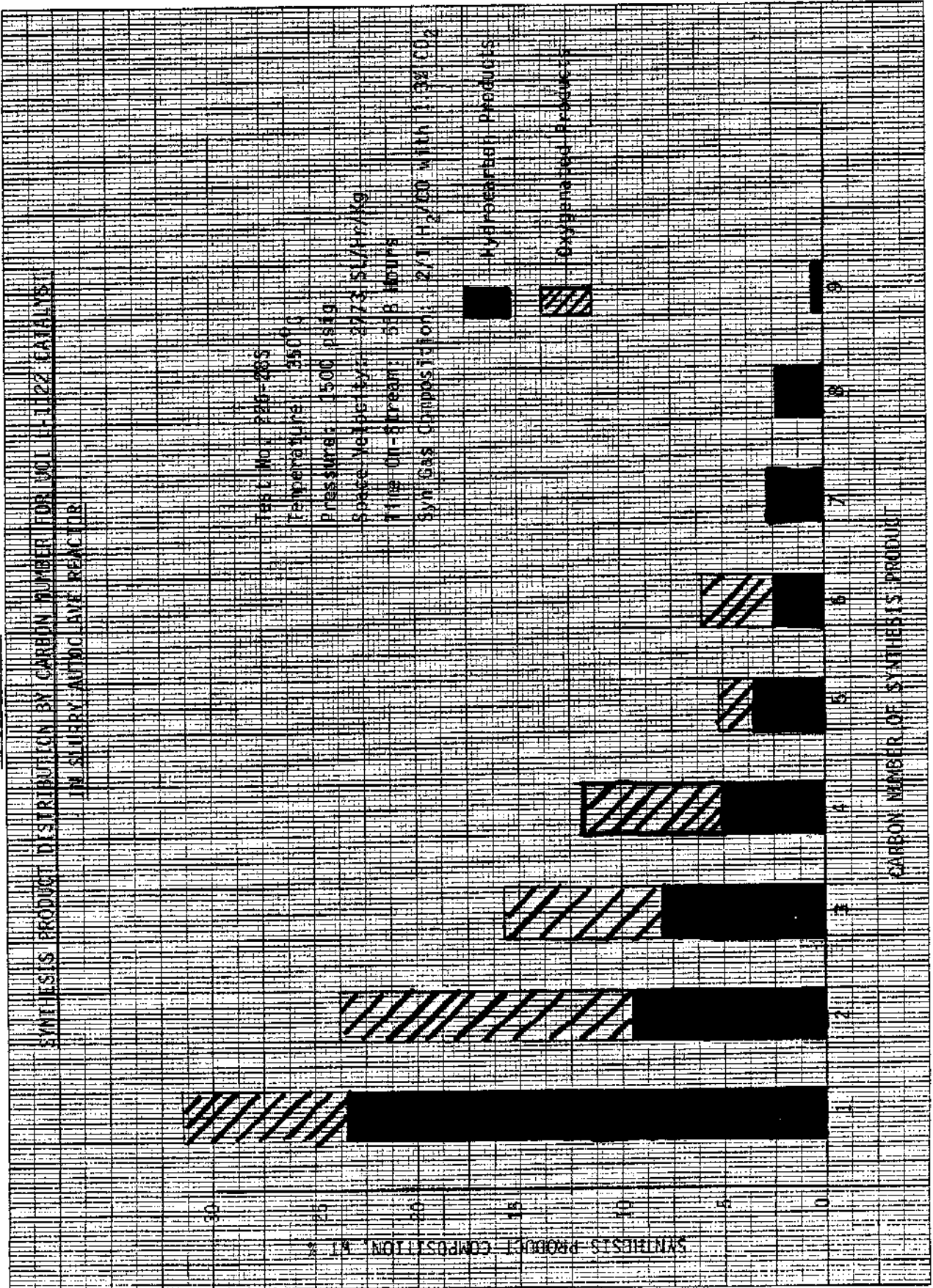


FIGURE VI-37



micro-metering pump rather than on a batchwise basis as in test 226-28S. The rate of oil addition ranged from 0.1 to 0.2 ml/min and was set to match the rate of collection of the hydrocarbon phase in the product separator. The oil inventory at the end of the run was found to be within five percent of the initial inventory using this method of oil make-up. Table VI-16 summarizes the operating conditions and results for the ten material balance periods made during the 361 hour test. Table VI-17 summarizes the crude ALKANOL compositions for each of the material balance periods.

During the initial 193 hours on-stream, a catalyst life test was performed at the following conditions:

Temperature:	350°C
Pressure:	2500 psig
Space Velocity:	3600 l/hr/kg
Agitator Speed:	720 rpm
Synthesis Gas Composition:	2/1 hydrogen/carbon monoxide with 10.8% carbon dioxide, 14.3% argon

These operating conditions were based in part on the high carbon monoxide conversions and selectivities to ALKANOLS observed at the 2500 psig reaction pressure in the previous slurry autoclave test. After about 193 hours on-stream, the reactor was shutdown to allow an inspection of the agitator assembly for possible mechanical problems. This inspection included briefly opening the reactor while a nitrogen purge was continued through the slurry. No mechanical problems were detected at this point or after the final shutdown. The run was continued for an additional 168 hours on-stream time using a synthesis gas of the following composition: 61.5% hydrogen, 8.4% argon, 28.8% carbon monoxide, and 1.3% carbon dioxide. During this second run period, reactor temperature was maintained at 350°C, while system pressure and space velocity were varied.

The catalyst performance observed during test 226-42S shows some unique trends not observed during previous tests using this catalyst. The cause of this behavior is thought to be related to the high partial pressures of

SUMMARY FOR RUN # 226-42 S

=====						
						TODAY'S DATE : 5/13/82

CATALYST NUMBER :	UCI L-1122					
ATOMIC FORMULA :	Proprietary					
PREP. METHOD :	UCI Prep					
SURFACE AREA(1) :	0	m ² /gm				
BULK DENSITY(1) :	4	gm/cc				
TEST NUMBER	1	2	3	4	5	6

TEST CONDITIONS :						
FEED H ₂ /CO Ratio	2.06	2.06	2.06	2.06	2.06	2.06
FEED CO ₂	10.80	10.80	10.80	10.80	10.80	10.80
Ave. Temp., °C	351.0	350.0	351.0	354.0	351.0	349.0
HOT SPOT, °C	351.0	350.0	356.0	359.0	351.0	350.0
PRESSURE, psia	2550.0	2500.0	2520.0	2530.0	2530.0	2530.0
WHSV, 1/hr/km cat.	3636.6	3656.6	3439.7	3452.1	3610.2	3969.8
HOURS on STREAM	22.3	48.0	75.6	96.8	164.5	190.0
CONVERSION :						
CO to Prods., vol%	24.86	22.50	17.36	16.34	10.26	11.93
CO to CO ₂ , vol%	0.13	-1.28	-1.04	-1.94	-0.84	-0.35
CO, gm mol/hr/km cat.	9.94	8.49	6.14	5.43	3.72	5.03
STY of Oxygenates(2)						
gm mol/hr/km cat.	8.64	7.17	5.01	4.47	2.83	3.51
STOICHIOM. H ₂ /CO converted	1.86	1.97	1.99	2.10	2.04	1.91
CARBON SELECTIVITY (Normalized Mol % on CO ₂ -free Basis) :						
CH ₃ OH	82.88	78.82	76.10	77.62	67.58	59.62
C ₂ -C ₆ ALCOHOLS	3.54	4.63	5.13	3.86	6.87	7.76
C ₂ -C ₆ ALD. & ESTERS	0.45	1.06	0.33	0.80	1.71	2.32
CH ₄	6.19	5.43	5.72	6.78	8.54	10.38
C ₂ -C ₃ HYDROCARBONS	1.88	1.70	2.51	3.30	5.42	7.59
C ₄ + HYDROCARBONS	5.14	8.36	10.22	7.56	9.96	12.33
APPROACH TO(3)						
WAS Equilibrium, °C :	37.4	44.7	-37.8	8.1	-48.7	0.7
CARBON ACCOUNTABILITY, % (4):	73.6	74.0	101.5	78.5	106.7	91.4
OXYGEN REJECTION RATIO, (5):	0.08	0.09	0.03	0.06	0.03	0.05

(1) Fresh, non-reduced catalyst.

(2) Space Time Yield (STY) = WHSV/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...

Table VI-16 (Concluded)

SUMMARY FOR RUN # 226-42S

CATALYST NUMBER : UCI L-1122
 ATOMIC FORMULA : Proprietary
 PREP. METHOD : UCI Prep.
 SURFACE AREA(1) : m²/gm
 BULK DENSITY(1) : 4 gm/cc

TODAY'S DATE : 5/13/82

TEST NUMBER	7	8	9	10
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TEST CONDITIONS :

FEED H ₂ /CO Ratio	2.14	2.14	2.14	2.14
FEED CO ₂	1.29	1.29	1.29	1.29
AVE. TEMP., °C	350.0	350.0	348.0	351.0
HOT SPOT, °C	350.0	350.0	349.0	351.0
PRESSURE, psia	1450.0	1470.0	2400.0	2410.0
WHSV, 1/hr/kam cat.	1600.0	1623.5	3373.7	2472.7
HOURS on STREAM	267.8	335.6	339.2	361.0
SHAFT SPEED, rpm :	720.0	720.0	720.0	720.0

CONVERSION :

CO to Prods., vol%	10.86	7.72	8.66	12.34
CO to CO ₂ , vol%	2.78	2.53	2.83	3.33
CO, gm mol/hr/kam cat.	2.64	2.14	4.64	4.98
STY of Oxygenates(2)				
gm mol/hr/kam cat.	1.74	1.29	3.21	3.25
STOICHIOM. H ₂ /CO converted	1.49	1.49	1.63	1.58

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

CH ₃ OH	52.68	48.03	59.97	54.59
C ₂ -C ₆ ALCOHOLS	11.55	10.30	8.29	8.91
C ₂ -C ₆ ALD. & ESTERS	1.48	1.87	1.18	1.70
CH ₄	7.93	9.11	7.45	7.67
C ₂ -C ₃ HYDROCARBONS	7.13	8.07	6.06	7.62
C ₄ + HYDROCARBONS	19.23	22.62	17.13	19.51

APPROACH TO(3)

WGS Equilibrium, °C :	79.6	-6.5	9.3	59.8
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CARBON ACCOUNTABILITY, % (4):	91.6	106.6	104.1	98.8
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OXYGEN REJECTION RATIO, (5):	0.14	0.05	0.06	0.12
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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 CO₂.

Table VI-17

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 226-42 S

Catalyst Number : UCI L-1122

Date : 1/5/82

Catalyst Formulation: Proprietary (UCI Catalyst) Wt% (H₂O FREE)

COMPONENT	TEST #					
	1	2	3	4	5	6
METHANOL	94.501	91.734	90.648	92.407	87.214	83.346
ETHANOL	.851	.580	.924	1.247	2.335	2.902
N-PROP OL	1.308	1.051	1.162	1.356	2.265	2.993
N-BUT OL	.147	.154	.159	.401	.578	.849
N-PENT OL	.000	.925	.189	.000	.000	.129
N-HEX OL	.270	.500	1.244	.000	.531	.150
ACET ALD	.000	.000	.000	.000	.172	.000
PROP ALD	.153	.081	.125	.157	.377	.596
BUT ALD	.143	.555	.103	.390	.750	1.268
PENT ALD	.000	.060	.000	.000	.000	.000
HEX ALD	.000	.000	.000	.000	.000	.000
C4 H.C.	.422	.447	.583	.839	1.208	1.872
C5 H.C.	.571	.505	.672	.976	1.499	2.324
C6 H.C.	.909	.904	.802	1.088	2.015	2.902
C7 H.C.	.198	1.612	1.794	1.085	.130	.293
C8 H.C.	.527	.879	.033	.041	.594	.167
C9 H.C.	.000	.009	1.561	.012	.333	.188
TOTAL	100.000	100.000	100.000	100.000	100.000	100.000
METHANOL	94.501	91.734	90.648	92.407	87.214	83.346
C2 - C6 ALCOHOLS	2.576	3.213	3.679	3.004	5.709	7.043
OTHER C2 - C6 OXYGENATES	.296	.697	.228	.548	1.299	1.864
C4 - C9 HYDROCARBONS	2.627	4.356	5.444	4.040	5.779	7.748
CALCULATED HIGHER HEATING VALUE Btu/gal	66164.	67813.	68462.	67107.	69118.	70676.

Continued...

Table VI-17 (Concluded)

CRUDE ALKANOL FUEL WT DISTRIBUTION

RUN 226-42 S

Catalyst Number : UCI L-1122

Date : 1/5/82

Catalyst Formulation: Proprietary (UCI Catalyst) Wt% (H₂O FREE)

COMPONENT	TEST #			
	7	8	9	10
METHANOL	75.858	72.825	81.425	77.849
ETHANOL	3.073	3.813	2.923	3.371
N-PROP OL	5.083	4.974	3.068	3.664
N-BUT OL	1.085	.836	1.032	.904
N-PENT OL	.430	.497	.273	.322
N-HEX OL	.831	.000	.000	.000
ACET ALD	.000	.249	.000	.215
PROP ALD	.283	.328	.180	.213
BUT ALD	.938	1.085	.669	.879
PENT ALD	.000	.000	.000	.105
HEX ALD	.000	.000	.000	.000
C4 H.C.	2.457	3.278	2.157	2.479
C5 H.C.	2.463	2.848	1.897	2.286
C6 H.C.	2.802	3.564	1.333	2.101
C7 H.C.	2.444	5.463	4.494	3.786
C8 H.C.	2.043	.215	.530	1.671
C9 H.C.	.209	.024	.020	.156
TOTAL	100.000	100.000	100.000	100.000
METHANOL	75.858	72.825	81.425	77.849
C2 - C6 ALCOHOLS	10.502	10.120	7.296	8.261
OTHER C2 - C6 OXYGENATES	1.222	1.662	.849	1.412
C4 - C9 HYDROCARBONS	12.418	15.393	10.430	12.479
CALCULATED HIGHER HEATING VALUE Btu/gal	74535.	75820.	72183.	73729.

carbon dioxide to which the catalyst was exposed during the first 193 hours of testing. As no improvement was seen upon reducing the carbon dioxide content of the synthesis gas, it appeared that the catalyst was irreversibly deactivated by exposure to high carbon dioxide partial pressures.

During the initial life test over the first 190 hours of on-stream time, the data in Figure IV-38 indicate an almost linear catalyst deactivation rate, as measured by carbon monoxide conversion, with on-stream time. It is believed that the high carbon dioxide partial pressures of 270 psig in the synthesis feed gas severely inhibited the ability of the catalyst to adsorb and therefore convert carbon monoxide. This is supported by the fact that the liquid-phase diffusivity of carbon dioxide at 270°C is almost twice that of carbon monoxide (21.6 vs. 11.6 mm²/hr) and the corresponding mass transfer coefficient is almost 50 percent greater⁽⁵²⁾. After the 200-hour campaign, the carbon dioxide-rich synthesis gas was replaced by one containing only 1.3 percent carbon dioxide and the reaction pressure was decreased to 1500 psig, thereby resulting in a carbon dioxide partial pressure of less than 20 psig. However, carbon monoxide conversions continued to decrease with on-stream time in line with the deactivation rate observed during the initial 150 hour test period. Furthermore, the carbon monoxide conversion levels under conditions of low carbon dioxide partial pressure were lower than those during the previous slurry autoclave test in which the carbon dioxide partial pressure in the synthesis gas never exceeded 30-35 psig. This can be seen in Table VI-18.

It would appear that the carbon dioxide inhibition of the L-1122 catalyst also affected the formation of the desired active catalyst species that promote C₂+ oxygenates production. Although ALKANOLS selectivities remained essentially constant at a value of 90 percent over the test duration (Figure VI-39), the observed ALKANOLS compositions differed greatly from those of the previous slurry autoclave test. The methanol content of the crude ALKANOLS (Figure VI-40) decreased by only about 15 percent from its initial value of 94.5 percent at 22 hours on-stream time. Previous tests with L-1122 catalyst resulted in large decreases in

TABLE VI-18

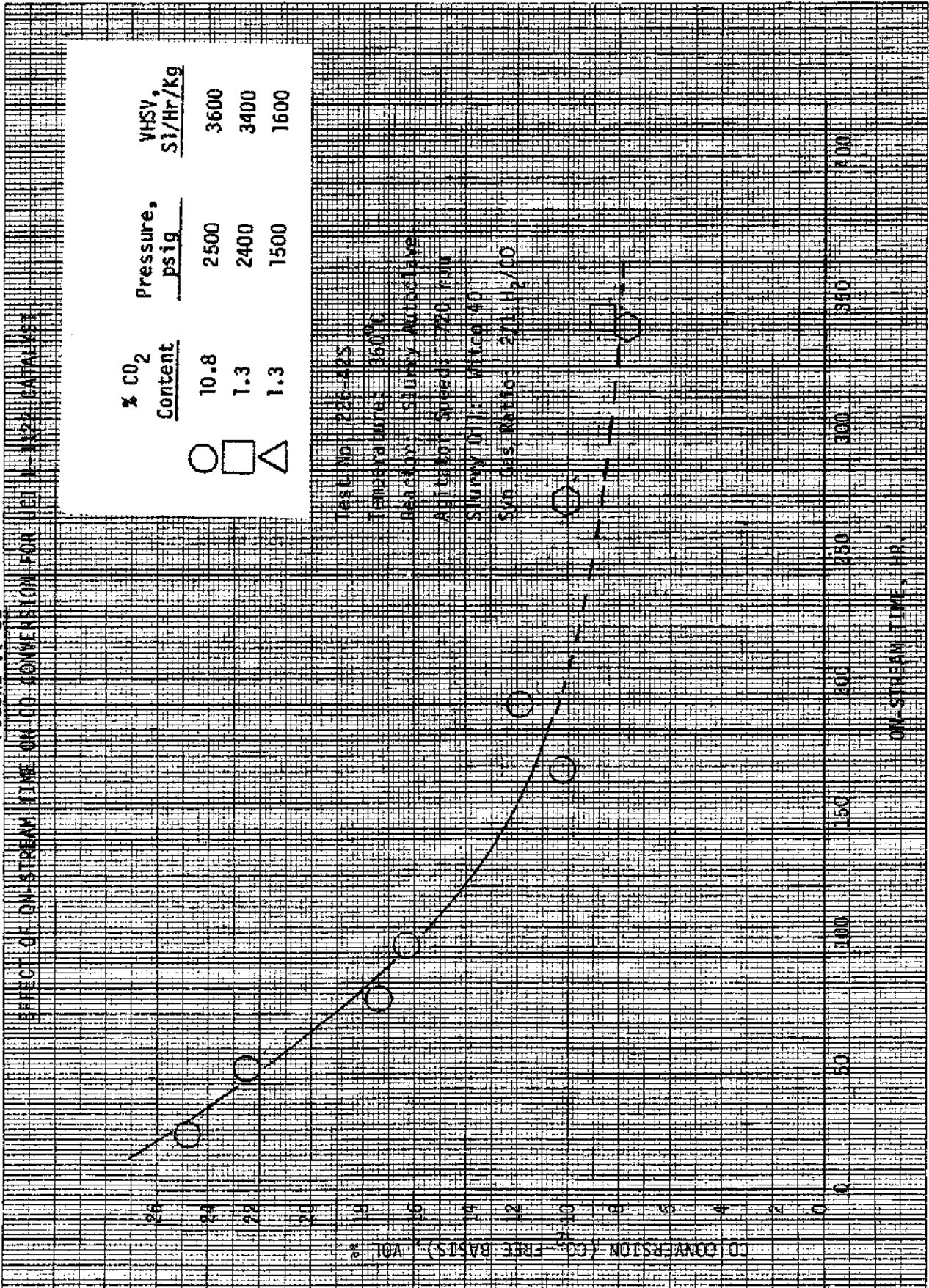
EFFECT OF CARBON DIOXIDE PARTIAL PRESSURE ON
L-1122 CATALYST ACTIVITY IN SLURRY AUTOCLAVE

	<u>Test 226-42S</u>	<u>Test 226-28S</u>
Maximum Carbon Dioxide Partial Pressure, psig	270	30-35
Percent Carbon Monoxide Conversion ⁽¹⁾	10.1; 7.7	20.9; 18.5
Catalyst Age, Hr.	268; 335	165; 436

(1) At 350°C; 1500 psig; 1600-1700 SL/hr/kg; 2/1 H₂/CO with 1.3%
CO₂; CO₂-free basis.

FIGURE VI-38

EFFECT OF ON-STREAM TIME ON CO CONVERSION FOR UFG-1132 CATALYST



% CO ₂ Content	Pressure, psig	VHSV, SI/Hr/Kg
10.8	2500	3600
1.3	2400	3400
1.3	1500	1600

Test No. 221-205
 Temperature: 350°C
 Reactor: Slurry Reactor
 Agitation Speed: 720 rpm
 Slurry In: Vitco 40
 SVR Gas Ratio: 2/1 (v/v)

FIGURE VI-39

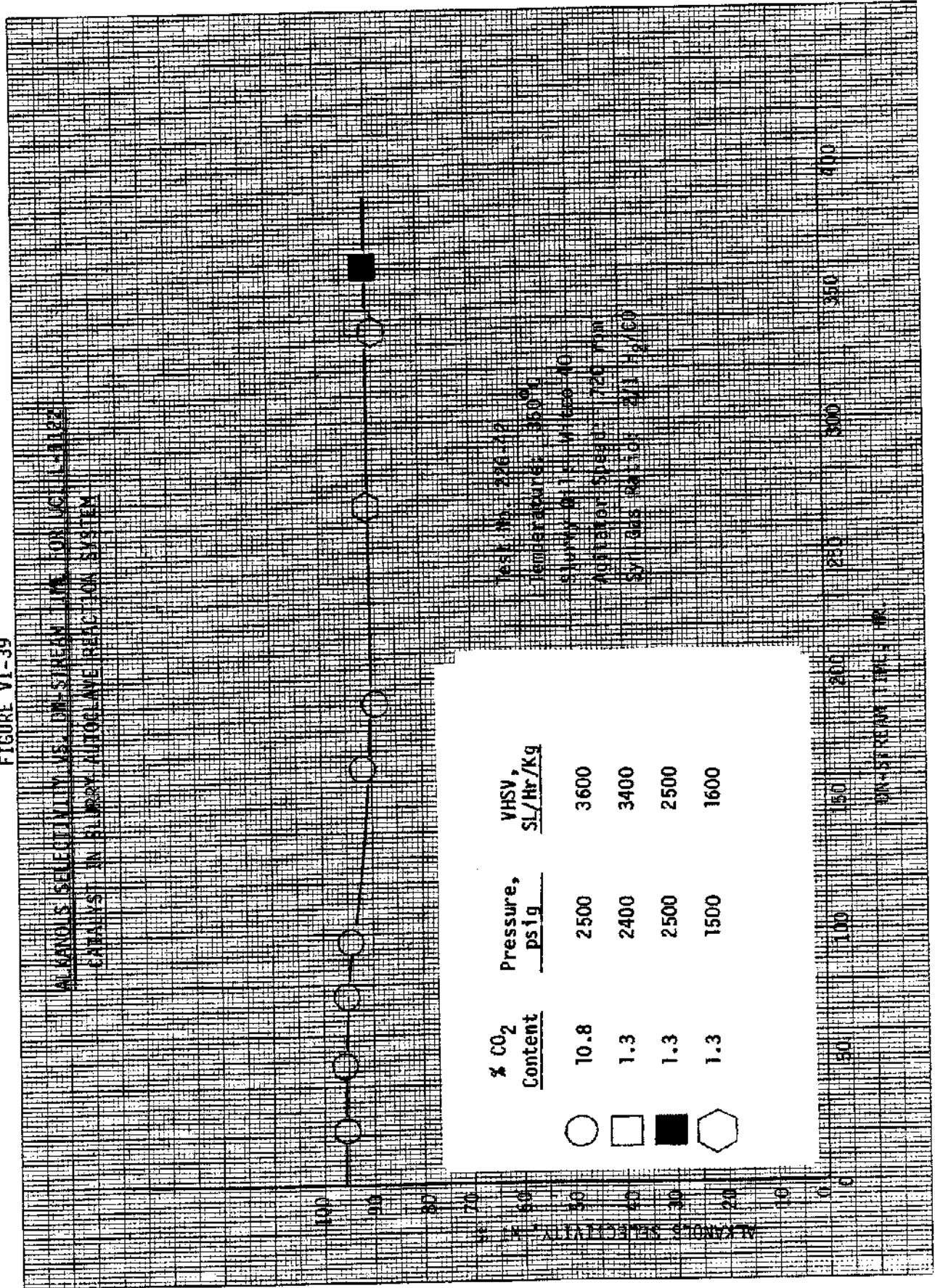
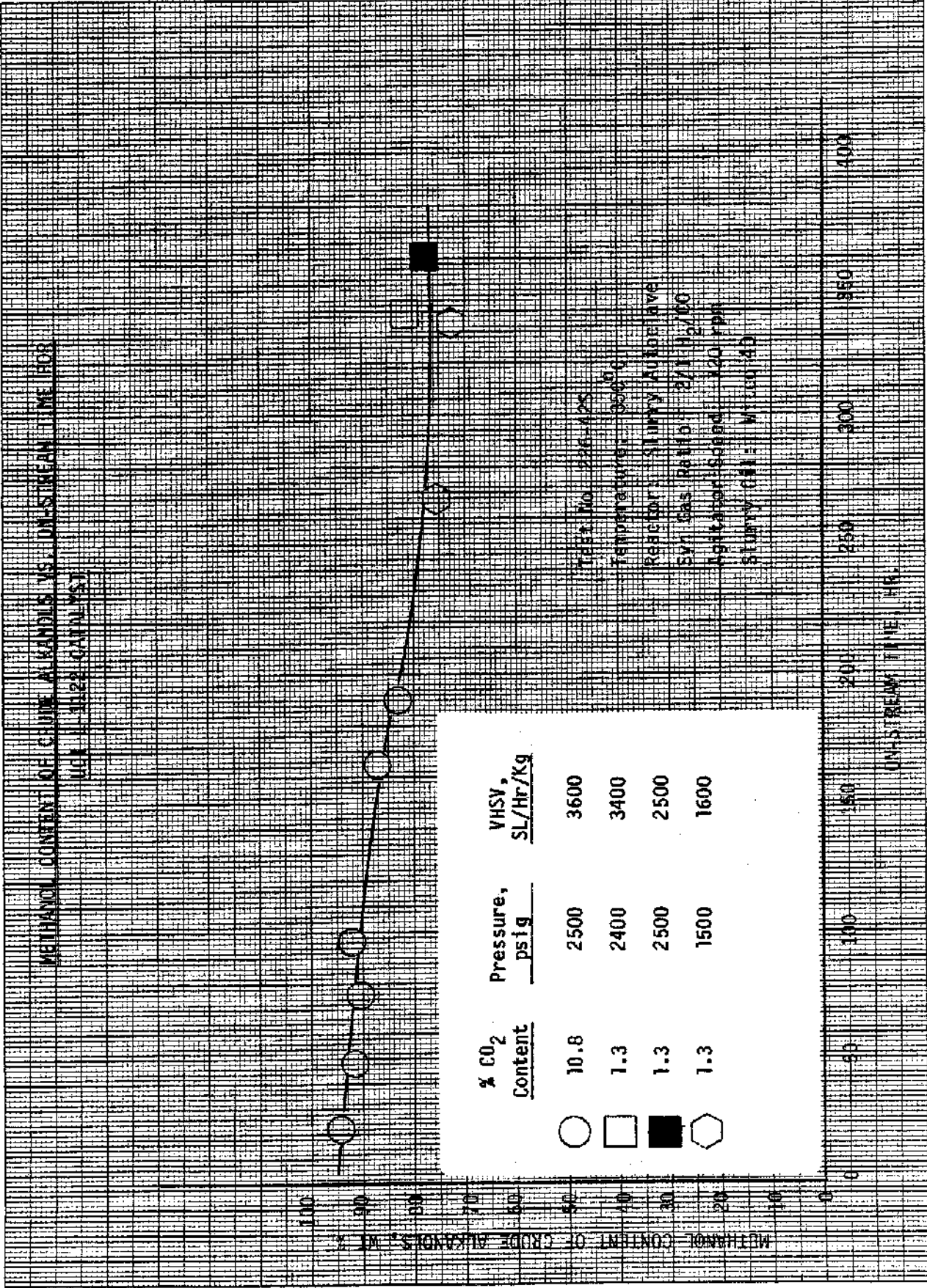


FIGURE VI-40



the methanol content of ALKANOLS to steady-state values ranging from 34 percent for the Berty reactor test and 18 percent for the slurry autoclave reactor test. These declines in methanol content resulted in corresponding increases in the C_2+ content of the ALKANOLS. However, in this current slurry-phase test, C_2-C_6 oxygenates increased only to about 10 percent (Figure VI-41) as compared to 42-57 percent for the previous L-1122 evaluations. At the end of the current 361-hour test, the C_4-C_9 hydrocarbon content (Figure VI-42) of the crude ALKANOLS did not stabilize and was still increasing at an apparently linear rate.

The product distribution by carbon number at the end of the test is shown in Figure VI-43 where it can be seen that the catalyst essentially performed as a methanol synthesis catalyst with the coproduction of about 10 percent (hydrocarbon-free basis) higher alcohols. The Schulz-Flory distribution was not applied to these data in view of the predominance of the methanol synthesis activity of the catalyst under the particular test conditions utilized.

FIGURE VI-41

CHLORINE OXYGENATES CONTENT OF CRUDE ALKALOIDS VS. ON-TREAM TIME FOR UNIT 11162Z CATALYST

% CO ₂ Content	Pressure, psig	VHSV, SL/Hr/Kg
10.8	2500	3600
1.3	2400	3400
1.3	2500	2500
1.3	1500	1600

TEST No. 1505-425
 TEMPERATURE: 350°C
 REACTOR: STUFFY AUTOFLAVE
 SV: 505 (BATH: 201) 1/1/00
 ACETONE: 5000 ml
 STUFFY (11162Z) 1000 (10)



CHLORINE OXYGENATES CONTENT OF CRUDE ALKALOIDS, WT %

ON-TREAM TIME, MIN

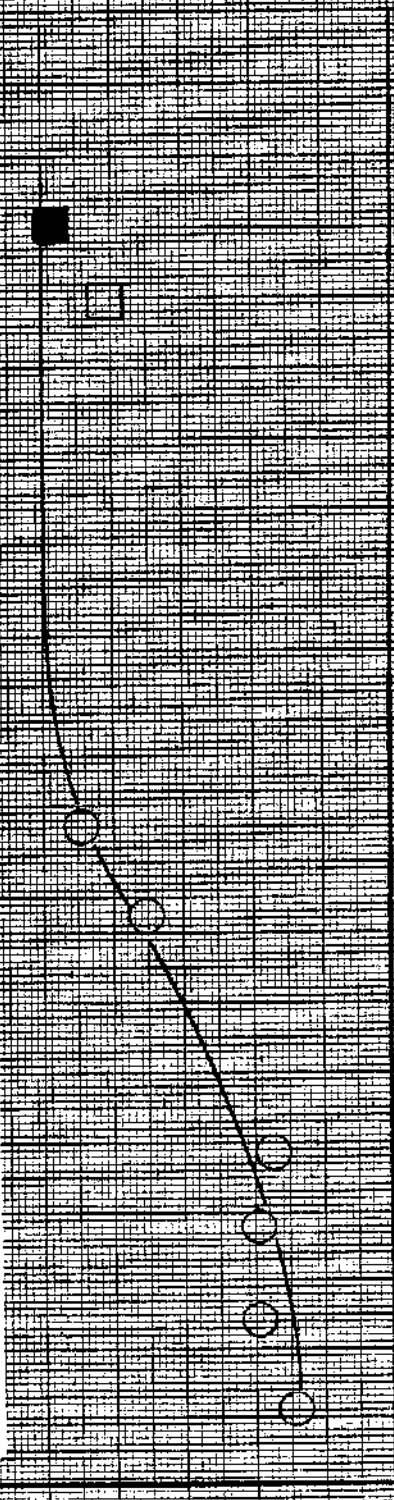


FIGURE VI-42

CO₂ HYDROCARBON CONTENT OF CRUDE ALKANOLS VS. ON-SSTREAM TIME FOR USE OF 1122 CATALYST

% CO ₂ Content	Pressure, psig	VHSV, SL/hr/kg
10.8	2500	3600
1.3	2400	3400
1.3	2500	2500
1.3	1500	1600

Test No. 225-APS

Temperature: 1500 F

Reactor: Stirring Autoclave

Syn Gas Rate: 18/1 1200

Agitator Speed: 720 rpm

Stirrer Int.: 11226 ALK

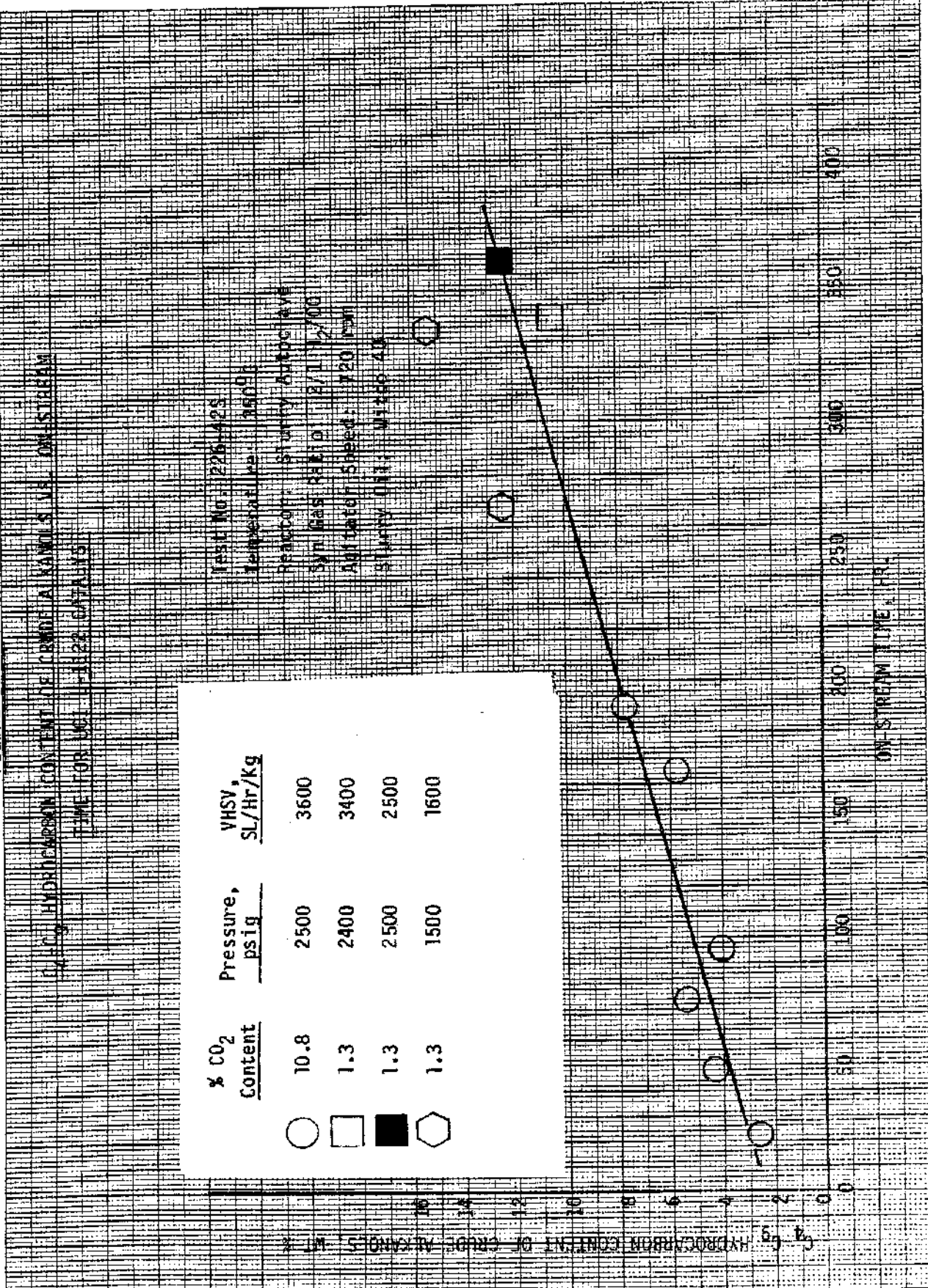
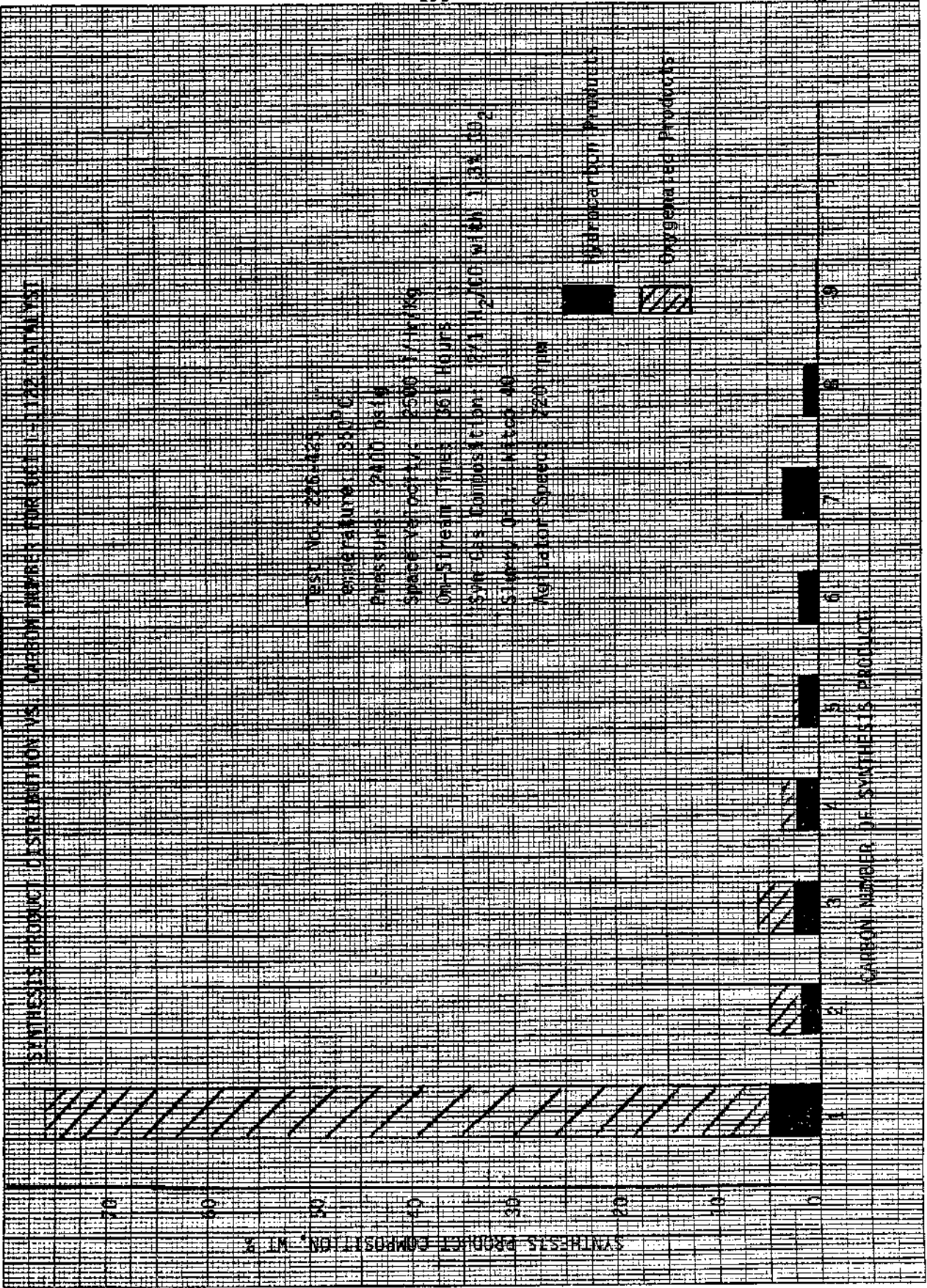


FIGURE VI-43



VII. DISCUSSION OF RESULTS OF CATALYST PERFORMANCE STUDIES (TASK 4)

The original work statement specified that the process variables studies (Task 2) as well as the catalyst performance studies (Task 4) be carried out in existing bench-scale (BSU) and process development (PDU) units only if it was determined that a liquid-fluidized reaction mode was applicable. If the ALKANOLS synthesis catalysts were judged to be better suited for another reaction mode, liquid-entrained or vapor-phase, then the BSU and the PDU should be appropriately modified.

One of the outcomes of the engineering studies of Task 3 was the identification of the liquid-entrained reaction system as a preferred mode for carrying out the ALKANOLS synthesis in a large-scale application. This finding was based on three premises: 1) a liquid-phase reaction system offers the potential for decreased production costs vis a vis the ability to efficiently recover the higher (with respect to methanol synthesis) heats of reaction of the ALKANOLS synthesis; 2) a liquid-entrained system utilizes a finely-divided slurry catalyst which provides a potentially higher catalyst productivity than that of a tableted or pelletized catalyst; and 3) the potential catalyst production cost savings foreseen for producing ALKANOLS catalyst in powdered form as opposed to tablets or extrusions.

In June, 1981, Chem Systems recommended to the DOE that a cost effective route of carrying out the process variables studies and catalyst performance studies would be to assemble a liquid-entrained, autoclave reaction system. A contract modification was approved and a 2-liter, stirred autoclave reaction system was assembled (see Section IV for details of the design of this unit). Based on data collected during the process variables studies, it was decided to initiate the catalyst activity maintenance test at the following reaction conditions:

Reactor Temperature:	350°C
Reactor Pressure:	2500 psig
Space Velocity:	3600 standard liters/hr/kg oxidized catalyst
Agitator Speed:	720 rpm
Slurry Concentration:	0.17 kg oxide/liter of oil
Oil Type:	Witco 40 mineral oil

Catalyst: UCI L-1122 pellets crushed and screened to 100 percent through U.S. 70 mesh.

Synthesis Gas Composition: 2/1 hydrogen/carbon monoxide with 10.8 percent carbon dioxide content.

Reduction Procedure: Vapor-phase, fixed-bed reduction using a 2 percent hydrogen in nitrogen mixture at 1 atmosphere, 900 SL/hr/kg space velocity with temperature programming from 200°C to 350°C over a 48 hour period.

The choice of these conditions was based on the high activity (75 percent total carbon monoxide conversion per pass) and the relatively high ALKANOLS productivity (13 gmmol/hr/kgm catalyst) observed in a previous test (#226-28S-4) made at these reactor conditions but with a 2/1 hydrogen/carbon monoxide synthesis gas having only 1.3 percent carbon dioxide content. The decision to utilize the higher carbon dioxide content synthesis gas in the catalyst activity maintenance test was based on the desire to approach the higher assumed steady-state carbon dioxide level used in the conceptual design study.

Upon introduction of synthesis gas, it was determined that the initial activity of the catalyst under these conditions was less than that observed for the previous test. Moreover, over the first 200 hours of operation, the rate of increase in the selectivity to the C₂+ components of the ALKANOLS with time was less than that observed for the previous test. The detailed discussion of the results of both tests is presented in Section VI.

Although the demonstration of catalyst activity maintenance in the slurry-phase reactor was never completed, a previous test in the Berty gradientless, vapor-phase reactor made over a 300-hour test period indicated that catalyst activity, as measured by both carbon monoxide conversion and ALKANOLS productivity, increased by more than 150% over that at 25 hours on-stream time.

VIII. DISCUSSION OF RESULTS OF ENGINEERING AND ECONOMIC STUDIES (TASK 3)

A. Overview

Throughout the performance of the experimental program, which was aimed at defining a preferred catalyst composition and reaction system, we have assessed the technical and economic applicability of this technology to the commercial-scale production of ALKANOL fuels. These assessments included the following major areas of investigation:

- Technical and economic advantages of utilizing ALKANOL fuels as synthetic transportation fuel or additives for conventional petroleum-based gasoline;
- Conceptual design of a commercial-scale facility for producing ALKANOL fuels from coal-derived synthesis gases; and
- Comparative economics of producing ALKANOL fuels, methanol and Mobil MTG synthetic gasoline from coal-derived synthesis gases.

The conceptual plant design was based on production of 1280 short ton/day crude ALKANOLS from coal-derived synthesis gases. This product rate is equivalent to an 1800 short ton/day methanol plant in terms of total energy content of synfuel product. It was assumed in the design study that a liquid-entrained reaction system would be utilized.

Although the process concept for producing ALKANOL fuels on a commercial-scale is in an early state of development, the techno-economic analyses performed to date are encouraging. The following key conclusions have been drawn:

- Production cost estimates (1981 Gulf Coast basis) indicate that ALKANOLS might be produced at relative costs to methanol and Mobil MTG of 1.15 and 0.86, respectively, when calculated on a constant product energy value basis. However, it should be

CHEM SYSTEMS I

realized that in all three cases about 84% of the respective product costs can be attributable to the cost of the coal-derived synthesis gases.

- An analysis of the value of ALKANOLS as a gasoline pool blending stock indicates that there are certain scenarios in which specific ALKANOL fuel compositions have refining values equivalent to or better than some of the current octane improvement methods used by petroleum refiners. One noteworthy example is the situation in which a refiner is adding toluene (valued at \$1.27/gal) to unleaded gasoline (88 Road Octane Number). The computed refining value of an ALKANOL fuel containing 20% methanol and 80% C₂-C₆ alcohols and having a measured blending value octane number (RdBVON) of about 125, when blended at the 10 weight percent level in unleaded gasoline, is about \$1.61/gal. Thus, these octane improvement economics calculations (1981 basis) suggest that there is a driving force between the estimated ALKANOLS refining value (\$1.61/gal) and the estimated ALKANOLS production costs (\$1.15/gal) for utilizing them as gasoline blending stocks.
- From a reaction engineering viewpoint, the ALKANOLS synthesis represents a compromise between the higher exothermicity/lower efficiency of the Mobil MTG process and the lower severity methanol synthesis process. Thus, the ALKANOLS synthesis has the potential to convert synthesis gases at a theoretical energy efficiency (i.e., Btu content of product divided by Btu content of synthesis gas assuming stoichiometric yields) intermediate between that of methanol (85.2%) and Mobil MTG gasoline (76.0%). Moreover, it appears that the ALKANOL mixtures have physical and chemical properties rendering them as potentially viable alternatives to petroleum-derived gasoline and gasoline octane improvers (e.g., toluene, t-butanol).

B. Conceptual Design of an ALKANOLS From Synthesis Gas Plant

1. Design Basis

A design basis for a conceptual facility to produce ALKANOL fuels from coal-derived synthesis gases was established based on the data generated in the vapor-phase test units and on our current understanding of the reaction chemistry and reaction engineering of the ALKANOLS synthesis. The objective of the conceptual plant design study was to determine the economic impacts of the reactor design and reactor operating conditions on the overall plant design thus providing the direction for generation of experimental data needed to define the preferred operating regime. Four key parameters (per pass carbon monoxide conversion, reactor outlet pressure, synthesis gas pressure, space velocity) were allowed to vary in an ensuing sensitivity analysis to determine their potential impact on the cost of production estimates. Other key parameters (e.g., ALKANOLS composition, synthesis gas composition, reactor design) were held constant, and although variations in these parameters could have a significant effect on the process economics, it was determined that the study of the effect of variations in the values of these parameters would best be performed at a future time when a stronger database would be available.

a. Design Parameters Kept Constant

• Synthesis Gas Composition

The reactor feed gas, which consisted of a fresh coal-derived synthesis gas component and a recycle gas component, was assumed to have a hydrogen/carbon monoxide ratio of 2.0/1 with 18 percent carbon dioxide content and 10% inerts (methane, ethane, light alcohol vapors, etc. derived from the ALKANOLS synthesis reactions). The composition of the inerts was computed from material balance and vapor/liquid equilibria calculations around the reactor loop. The 18 percent carbon dioxide level corresponded to equilibration of the water-gas shift reaction at the outlet of the reactor. Although the process variables study indicated that high carbon dioxide levels in synthesis gas may adversely affect

catalyst activity, it was decided in this preliminary design to circumvent the added costs of a carbon dioxide-scrubber for the reactor effluent gases by allowing the carbon dioxide in the recycle gases to achieve a steady-state level. This required an increased purge in order to satisfy the material balance around the synthesis loop.

The fresh coal-derived synthesis gas was assumed to have a 2/1 hydrogen/carbon monoxide ratio and contain 5.5 percent carbon dioxide. This type of gas could come from coal gasifiers based on slagging partial oxidation technology in which no hydrocarbons (e.g., methane) are produced, and the raw gas is shifted and scrubbed to achieve the hydrogen/carbon monoxide ratio and carbon dioxide levels assumed (low levels of nitrogen/argon normally associated with oxygen-blown gasifiers were neglected in this study).

In the process variables scans performed after the initiation of the conceptual design study, it was determined that synthesis gas composition at the reactor inlet could have a significant effect on catalyst performance. However, a sensitivity analysis of the effect of synthesis gas composition on overall process economics was not performed and should be included as a key task in any future techno-economic assessment efforts.

- Product Yield Spectrum

The product yield spectrum was based on the results of tests made in the Bertly vapor-phase reactor during the early phases of the process variables scans. The overall product composition assumed in the study consisted of 9.0 wt percent light (C₁-C₃) hydrocarbon gases, 69.3 wt percent alcohols and 21.7 wt percent gasoline-range hydrocarbons, all expressed on a water-free basis. The carbon number distribution for each product class is shown in Table VIII-1. In practice, we detected small quantities of oxygenates such as aldehydes and ketones which have been included in the general product class defined as alcohols. In a large-scale plant, a hydrogenation finishing reactor might be required to convert any aldehydes to alcohols. Commercial catalysts and processes (e.g., cobalt catalysts in the OXO Process) are readily available for this step. A raw ALKANOLS finishing step has not been included in this study. Depending upon

TABLE VIII-1

CARBON NUMBER DISTRIBUTION FOR ASSUMED PRODUCT SLATE

Alcohols, Wt%

C ₁	45.1
C ₂	22.7
C ₃	15.4
C ₄	6.3
C ₅	7.9
C ₆	<u>2.6</u>
Total	100.0

Gasoline-Range Hydrocarbons, Wt%

C ₄	33.7
C ₅	18.4
C ₆	16.1
C ₇	10.6
C ₈	8.3
C ₉	9.7
C ₁₀	<u>3.2</u>
Total	100.0

Light Hydrocarbon Gases, Wt%

C ₁	60.0
C ₂	26.7
C ₃	<u>13.3</u>
Total	100.0

catalyst composition and reaction conditions, the composition of the hydrocarbon (C₄+) fraction also varies, and we have detected paraffins, both normal and iso, as well as olefins. In this study, it was assumed that all C₄+ hydrocarbons were n-paraffins. Thus, the crude ALKANOLS fraction, after separation of product water and light hydrocarbon gases, would have the following composition:

Methanol	-	34.3 wt percent
C ₂ -C ₆ Alcohols	-	41.9
C ₄ -C ₁₀ hydrocarbons	-	23.8

● Reactor Design

Chem Systems⁽⁵³⁾ has been developing technology for the synthesis of methanol utilizing a three-phase reaction system in which a finely divided, methanol synthesis catalyst is entrained in an inert circulating oil. In this way, the exothermic heat of reaction can be efficiently removed by generating steam either in an external heat exchanger or in tubes immersed within the liquid-entrained reactor. In this current study, we assumed the utilization of a liquid-entrained reactor system for the ALKANOLS synthesis in which a high boiling (e.g., C₁₇-C₂₅) mineral oil was assumed as the inert circulating oil. Although the ALKANOLS synthesis product slate was based on experimental data obtained in a vapor-phase, gradientless reactor, later data obtained in the slurry-phase autoclave system indicated that a liquid-entrained reaction mode has the potential to generate a similar product slate as that observed in the back-mixed, vapor-phase reactor.

The exothermic heat of the ALKANOLS synthesis reactor was assumed to be recovered as high pressure steam in an external heat exchanger on the circulating oil loop. Although 400 psig steam was produced, it may be possible to generate steam up to 900 psig, which could be used to drive steam turbines instead of providing heat for the ALKANOLS product distillation train. However, a steam/electricity balance has not been optimized in this preliminary design study.

The superficial gas velocity in the reactor was assumed to be about 0.5 ft/sec. The slurry density or catalyst loading was assumed at 2.5 lb of oxidized catalyst per gallon of circulating oil.

- Reactor Temperature

The conceptual design was based on experimental data obtained at 350°C (662°F) isothermal reactor temperatures. In the large-scale equipment, the exothermic reactions are carried out adiabatically. Based on the flowrates of feed gas and circulating oil and on the calculated heat of the ALKANOLS synthesis reactions, a 29°C (52°F) temperature rise was taken across the reactor. Thus, in order to maintain the 350°C reactor outlet temperature, the feed gas and circulating oil inlet temperatures were maintained at 321°C (610°F).

- Product Recovery Train

Once the primary vapor/liquid separation has been achieved, a two-phase hydrocarbon/aqueous alcohols separation is made. The hydrocarbon phase can either be sent to storage or held in a holding tank for blending with the dried alcohols fraction to produce the crude ALKANOLS product. The design of the aqueous alcohols separation is based on a process described⁽⁵⁴⁾ by the Institute Francais du Petrol (IFP). This dehydration scheme is based on the use of diethylene glycol as a solvent and combines extractive distillation technology with hetero-azeotropic distillation.

- Plant Capacity

The nominal design capacity was 1280 short ton/day (stpd) crude ALKANOLS (water-free) with an 8000 hour per year stream factor. This capacity was selected to give a product energy production rate equivalent to that of an 1800 stpd methanol plant. The assumed net synthesis gas flow (total synthesis gas flow to reactor less purge gas) to produce the specified yield of crude ALKANOLS was 2013 million Btu/hr. This value is about 13 percent higher than that of the equivalent 1800 stpd methanol plant with

the differences emanating primarily from product quality differences (methanol has about a 30% lower volumetric energy content than that of the crude ALKANOLS).

b. Design Parameters Sensitized

• Carbon Monoxide Conversion Per Pass

The base case carbon monoxide conversion was assumed to be 22% per pass to products (at zero selectivity to carbon dioxide). Production cost estimates were also made at carbon monoxide conversions per pass of 30% and 40%, respectively, while assuming the same product slate as for the base case conversion. Overall carbon monoxide conversion was fixed at 86.8%.

• Reactor Outlet Pressure

The base case reactor outlet pressure was assumed to be 2050 psia with an equivalent partial pressure of carbon monoxide and hydrogen of 1475 psia. The 575 psia differential is attributable to the carbon dioxide and inerts (CH_4 , C_2H_6 , CH_3OH , etc.) content of the recycle gases. Production cost estimates were also made at a lower reactor outlet pressure of 1550 psia which is essentially equivalent to that utilized in the autoclave tests.

• Synthesis Gas Feed Pressure

The base case synthesis gas feed was assumed to be delivered to the ALKANOLS plant battery limits at a pressure of 550 psia. A two-stage, compressor was then used to compress the synthesis gas to the ALKANOLS synthesis loop pressure. This compressor and its associated power requirements can represent a significant portion of the cost of production of the ALKANOLS. A production cost estimate was made to determine the effect of higher synthesis gas delivery pressure, namely 1040 psia.

- Space Velocity

The base case space velocity was assumed to be 3000 standard liters/hr/kg of catalyst at the specified base conditions of temperature and pressure. A product cost estimate was also made to determine the effect of operating at the higher space velocity of 6000 standard liters/hr/kg catalyst.

2. Process Description

A process flowsheet for the conceptual 1280 stpd ALKANOLS plant has been developed. The ALKANOLS synthesis loop is shown in Figure VIII-1, and the ALKANOLS product dehydration section is shown in Figure VIII-2. A material balance indicating the flow rates of the major streams in both plant sections is presented in Table VIII-2.

In the synthesis loop, makeup synthesis gas derived from a coal gasification facility in which the raw gas has been shifted and scrubbed to maintain a 2.118 hydrogen/carbon monoxide ratio with a residual carbon dioxide content of 5.5% is compressed to 2100 psig. The thus compressed synthesis gas is blended with the recycle gas recovered from the vapor/liquid separator V-101 and heat exchanged against the hot reactor effluent stream in feed preheater H-103. The preheated blended synthesis gases are fed to seven parallel synthesis reactors where they are contacted with a circulating stream of inert hydrocarbon oil containing the active methanol synthesis catalyst. For the current conceptual design, a catalyst loading of 0.3 kg/liter of oil was assumed, and the oil circulation rate was 2500 gpm per reactor, which is equivalent to a feed gas/oil volumetric ratio of about 34/1. At this ratio and the assumed exothermic heat liberated per pass by the ALKANOL synthesis reactions, the calculated temperature rise across the reactor was 52^oF (29^oC). The hot oil is circulated to a heat exchanger, HE-101, where it is cooled while generating 400 psig steam. Each reactor is 8 feet in diameter by 150 feet long and fabricated from stainless steel-clad carbon steel. The assumed circulation rate corresponds to a superficial velocity of about 0.1 ft/sec.

TABLE VIII-2
MATERIAL BALANCE FOR CONCEPTUAL PLANT DESIGN

COMPONENT IN	(1) FRESH FEED	(2) REACTOR FEED	(3) REACTOR EFFLUENT	(4) OFF GAS	(5) PURGE	(6) RECYCLE	(7) LIQUID PRODUCT	(8) VENT	(9) PARAFFIN ALCOHOL PRODUCT	(10) NET ALCOHOL PRODUCT	(11) SOLVENT	(12) LIGHT ALCOHOLS PRODUCT	(13) REGENERATION COL- UM FEED	(14) HEAVY ALCOHOL PRODUCT	(15) WATER PRODUCT
CO	20	7,489.7	29,192.7	22,772.1	504.1	21743.0	43.2	43.2	-	-	-	-	-	-	-
H ₂	2	15,776.9	58,305.4	44,536.2	1,927.7	42,608.5	59.6	59.6	-	-	-	-	-	-	-
CO ₂	44	1,358.9	21,894.0	21,463.7	928.6	20,535.1	430.3	390.0	-	40.3	-	40.3	-	-	40.3
H ₂ O	18	80.5	4,373.0	84.2	3.7	80.5	4,208.8	13.0	3	4,272.0	194.0	4,466.0	-	-	4,272.0
CH ₃ OH	32	502.8	1,074.0	629.7	26.9	602.8	1,244.3	38.7	-	1,205.6	-	1,205.6	-	-	-
C ₂ H ₅ OH	46	129.9	575.1	135.9	6.0	129.9	439.2	6.0	-	432.4	-	432.4	-	-	-
C ₃ H ₇ OH	60	34.0	268.3	25.6	1.6	34.0	230.7	0.7	-	230.0	-	230.0	-	-	-
C ₄ H ₉ OH	74	6.4	83.0	6.6	0.2	6.4	76.4	0.1	-	76.3	-	76.3	-	-	72.5
C ₅ H ₁₁ OH	88	7.5	84.1	7.8	0.3	7.5	76.3	-	-	76.3	-	76.3	-	-	76.3
C ₆ H ₁₃ OH	102	0.6	24.0	0.6	-	0.6	23.4	-	-	23.4	-	23.4	-	-	23.4
CH ₄	16	6,507.0	8,946.0	8,892.1	385.1	8,507.0	53.9	52.7	1.2	-	-	-	-	-	-
C ₂ H ₆	30	1,359.0	1,463.3	1,420.7	61.7	1,359.0	42.6	37.0	5.6	-	-	-	-	-	-
C ₃ H ₈	44	384.0	419.6	401.5	37.5	384.0	18.1	12.5	5.6	-	-	-	-	-	-
C ₄ H ₁₀	58	715.7	877.6	740.1	32.4	715.7	123.5	54.9	74.6	-	-	-	-	-	-
C ₅ H ₁₂	72	230.6	311.0	249.4	10.8	230.6	61.6	13.6	40.0	-	-	-	-	-	-
C ₆ H ₁₄	86	96.1	149.1	100.3	4.2	96.1	48.8	5.5	43.3	-	-	-	-	-	-
C ₇ H ₁₆	100	20.4	50.5	21.3	0.9	20.4	29.2	1.4	27.8	-	-	-	-	-	-
C ₈ H ₁₈	114	10.7	31.1	11.1	0.4	10.7	20.0	0.5	19.5	-	-	-	-	-	-
C ₉ H ₂₀	128	7.0	20.3	7.2	0.2	7.0	21.1	-	21.1	-	-	-	-	-	-
C ₁₀ H ₂₂	142	1.5	7.9	1.6	0.1	1.5	6.3	-	6.3	-	-	-	-	-	-
Di ethyl benzene															
glycol 105											1,614.5				
Total															
LN Holes/HR	29,585.5	121,673.8	108,824.0	101,080.7	4,392.4	97,088.1	7,343.3	771.8	256.0	6,356.3	1,800.5	1,871.8	6,293.0	172.2	4,312.3

CONCEPTUAL ALKANOLS SYNTHESIS LOOP

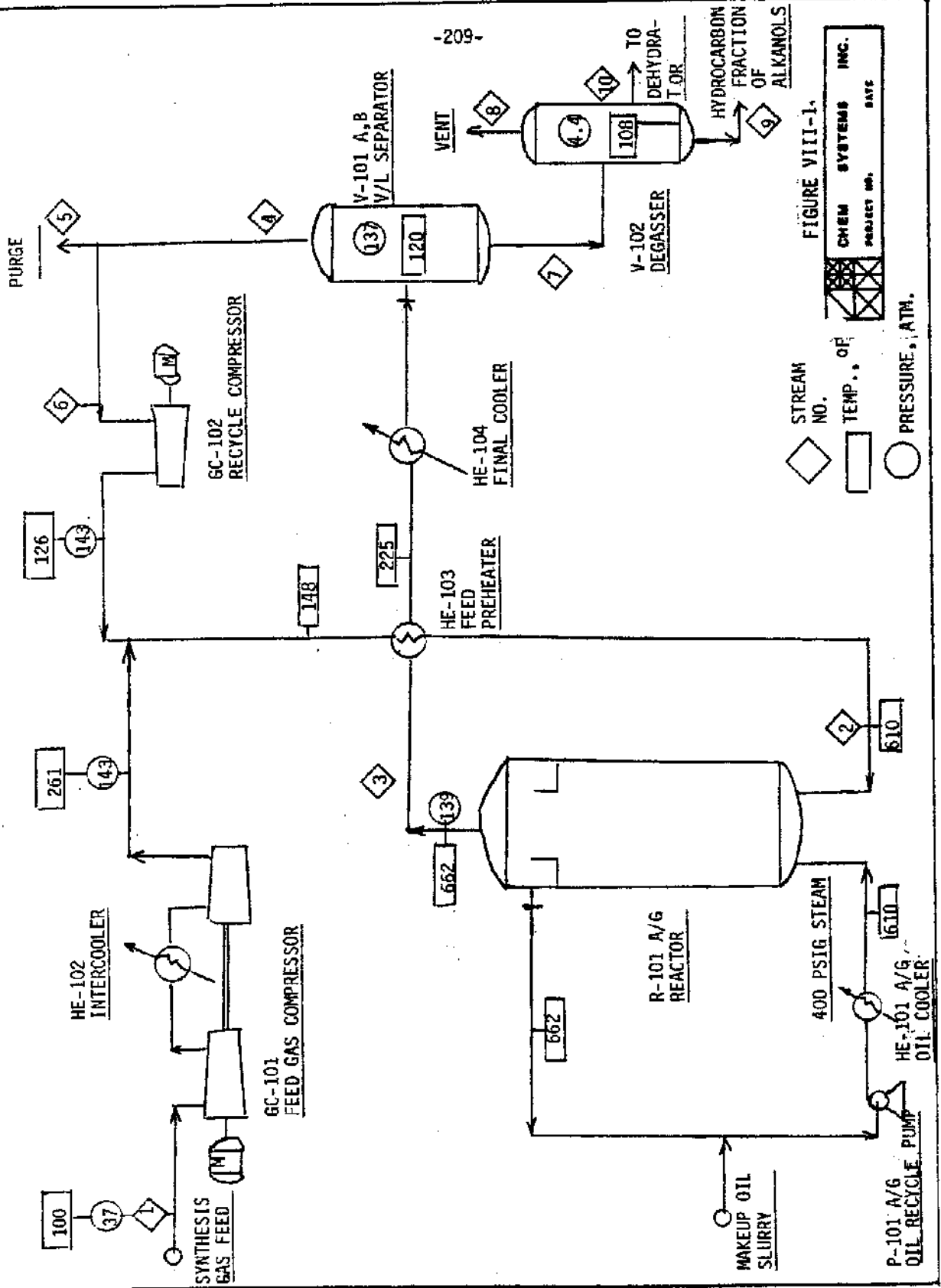


FIGURE VIII-1.

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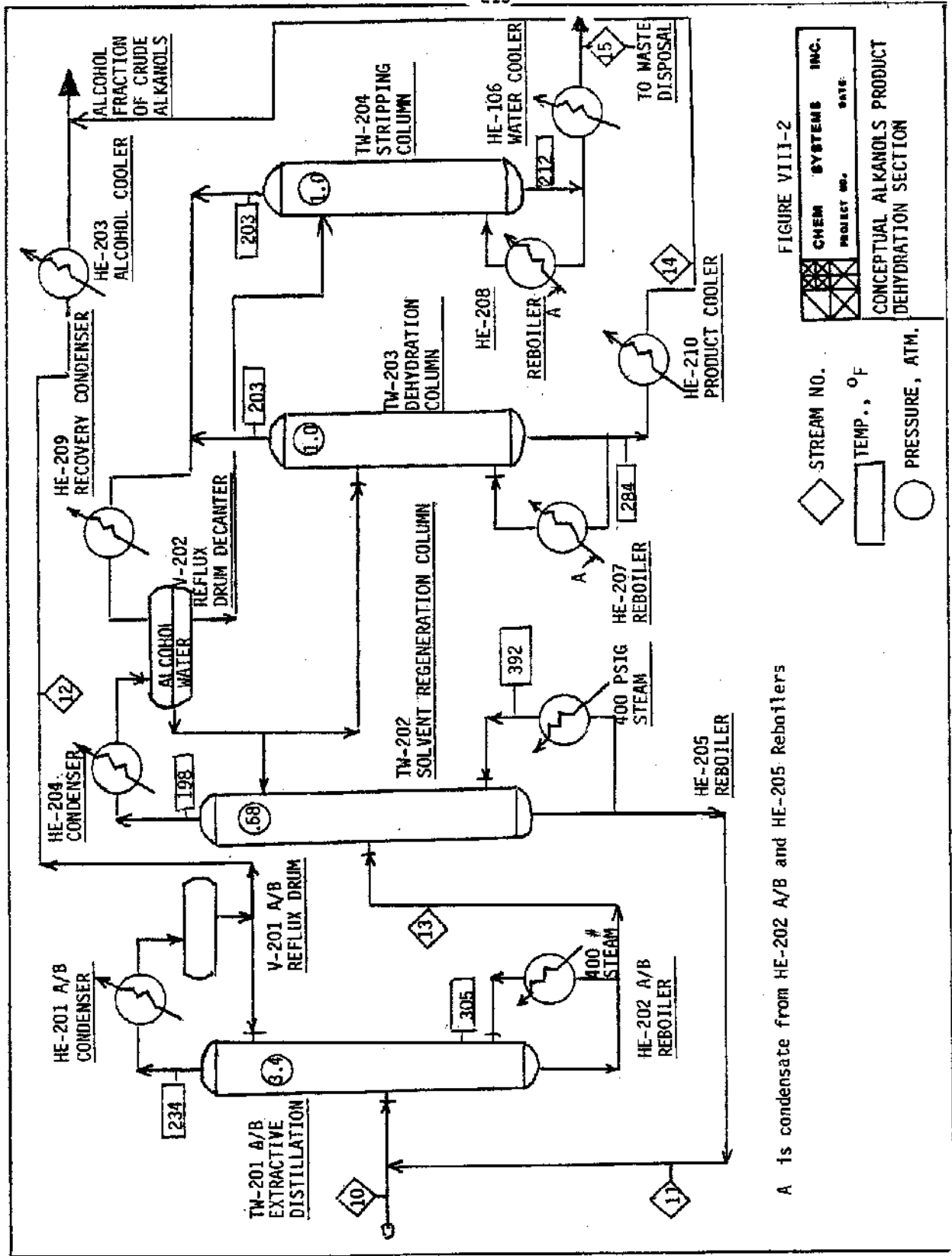


FIGURE VIII-2

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 CONCEPTUAL ALKANOLS PRODUCT
 DEHYDRATION SECTION

◊ STREAM NO.
 ◻ TEMP., °F
 ○ PRESSURE, ATM.

A is condensate from HE-202 A/B and HE-205 Reboilers

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The reactor effluent is then heat-exchanged against reactor feed gas and further cooled in the final cooler, HE-104, to 120°F to condense product and water. Condensed liquid products and unconverted gas are separated in the vapor/liquid separation drum, V-101. The unconverted gas is recompressed to 2,100 psig via the recycle compressor, GC-102 and returned to the reactor feed stream. A small purge stream is taken from the vapor/liquid separator to prevent the buildup of methane and other gaseous byproducts in the synthesis reactors. Liquid products from the separator are depressurized to about 50 psig in the degasser, V-102, to remove dissolved gases from the product. The gases are vented to the atmosphere.

The C₄+ hydrocarbons and alcohol-water products phase separate in the degasser. The hydrocarbon phase is sent to storage, and the alcohol-water layer goes to a multi-tower distillation train for the removal of water. Except for methanol, all of the alcohols form azeotropes with water, thus making it necessary to use a solvent for extractive distillation. The dehydration scheme is based on use of di-ethylene glycol (DEG) as a solvent and the combination of extractive distillation and heteroazeotropic distillation. First, the product alcohol-water mixture and DEG are fed to the extractive distillation column, TW-201. In this column, the lighter alcohols (C₁, C₂, C₃) go overhead and the heavier alcohols, water and the solvent bottoms are fed to the solvent regeneration column, TW-202. Due to high vapor rates, two parallel extraction columns are required. In the regeneration column, the alcohol-water mixture is distilled overhead and the solvent bottoms (containing some water to reduce the bottoms temperature) are recycled back to the extraction column.

Because of the limited solubility of higher alcohols and water, the product phase separates in the regeneration column reflux drum, V-202. The alcohol-rich phase is sent to the dehydration column, TW-203, for further purification. The bottoms, containing C₄, C₅ and C₆ alcohols, are cooled in product cooler HE-210 and sent to product storage. The overheads containing an azeotropic mixture are recycled back to the phase separator. The water-rich phase is sent to the stripping