APPENDIX C

CATALYST TESTING

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CONTENTS

INTRODUCTION TO TASK 1 TESTING

This past year has seen the Task 1 testing program change significantly. A year ago we had just started Task 1 testing, using methanol as the feedstock. At the reaction conditions used, methanol produced a highly aromatic product. Due to the backmixing in the Berty reactor, the aromatics produced were all highly methylated yielding a solid condensed product. LZ-105-6 produced significant quantities of durene. Operating problems with reactor plugging and accurate collection and analysis of these solid products naturally resulted. Also, methanol is not a major intermediate in Fischer-Tropsch synthesis, while small olefins are F-T products and proposed intermediates. (The SSC doe not have to break the C-O bond; the metal component will do that). Thus, propylene was chosen to replace methanol as the Task 1 feedstock, since it is the smallest olefin with reactivity similar to the larger olefins.

Unlike methanol, propylene has served well as a Task 1 feedstock. During the past year, the Task 1 testing has been very successful. Not only has much been learned about the reactivity of the molecular sieves which will be useful in Task 2, but a superior Task 1 catalyst has been identified.

Data from Task 1 tests in the last quarter are given below, followed by a summary of all Task 1 work. The data presentation for this report is similar to that in the previous report except for presenting simulated distillation data. In previous reports the simulated distillation of only the condensed liquid, ASTM D-2887, was presented. In this report the liquid distillation data is combined with gas phases data. The C_5 and C_6 gas phase components are divided into iso and normal, paraffins and olefins. The backflush heavies peak is divided into C_7 and C_{10} components. All these components are assigned appropriate boiling points and added to liquid product data to give a total C_5^+ breakdown.

Sufficient knowledge of the reactivities of the molecular sieves is understood to proceed with Task 2. Task 1 has served its purpose and no further Task 1 testing is planned at this time.

ZSM-5, Runs 9972-18 and 9972-20

ZSM-5 is a well-known catalyst for the conversion of both methanol and small olefins to gasoline range products. Catalysts with this crystal structure are the standard against which new promising catalysts should be compared.

With this in mind, two ZSM-5's were synthesized and tested for Task 1 activity. In run 9972-20, a ZSM-5 with a SiO_2/Al_2O_3 ratio of 35 was tested. This SiO_2/Al_2O_3 is similar to that of LZ-105-6 which was tested previously in run 9972-13. In run 9972-18 ZSM-5 of a higher SiO_2/Al_2O_3, 85, was tested.

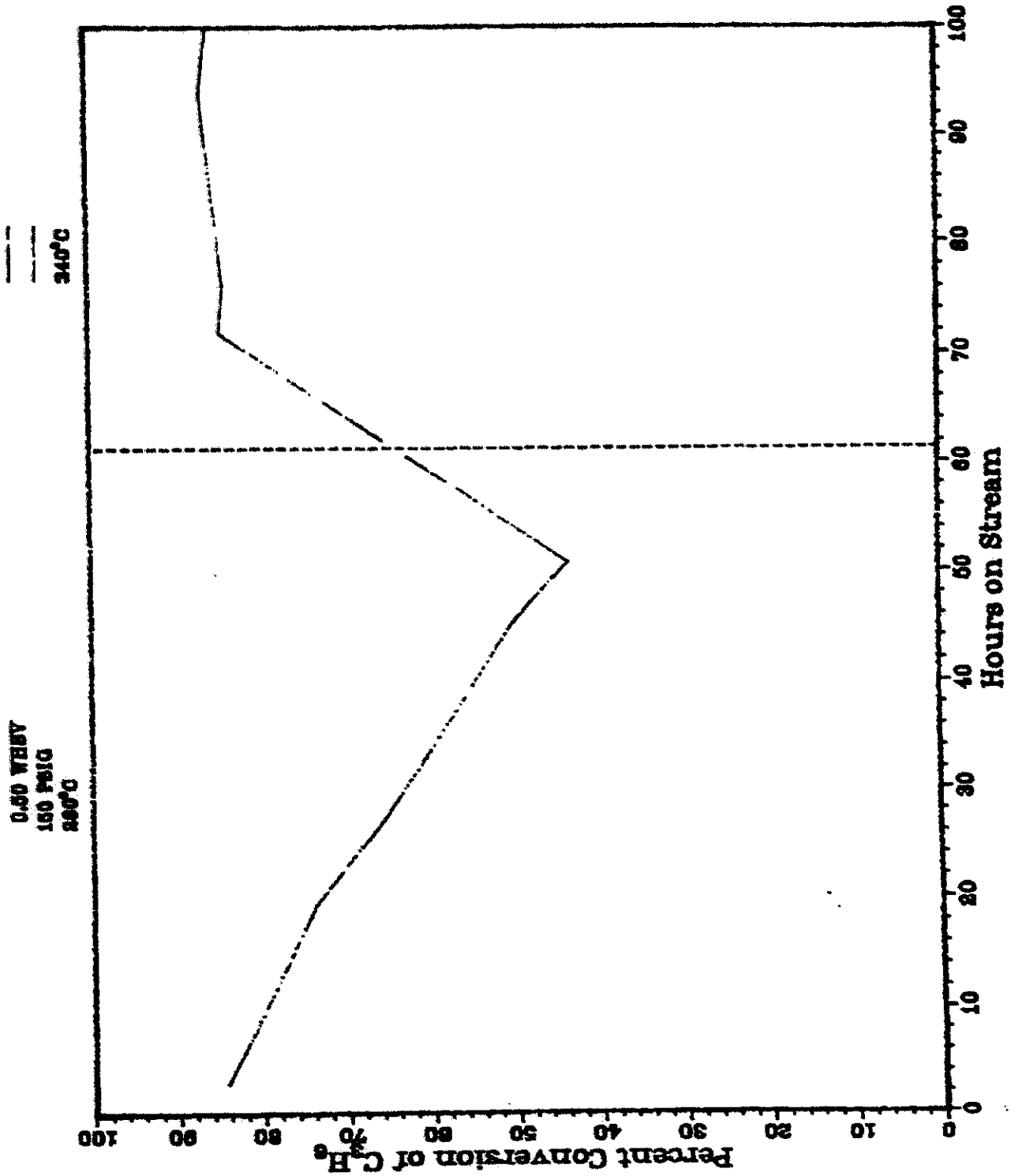
Plots of the conversion and product selectivity data for runs 9972-18 and 9972-20 are shown in Figures 1 to 4. Tables 1A, 1B, 2A and 2B contain the detailed material balances and product selectivity. The results from these runs should be compared to those of run 9972-13, which was reported last quarter. The conversion and product selectivity for this run are shown in Figures 5 and 6. The three catalysts all show stable operation at 340°C both in conversion and product selectivity. The higher silica/alumina ratio ZSM-5 did not show stable operation at 280°C. This temperature would seem to be inadequate to effectively desorb the products from the catalyst. The products may block the active sites leading to lower activity. This site-blocking should be more of a problem with the higher silica alumina ratio ZSM-5 which has fewer active sites. 340°C seems to be adequate to desorb the products or intermediates from the active sites.

Under the conditions employed, these catalyst did not produce the large quantities of propane and butane which were seen with LZ-105-6 at higher temperatures. The C_4's which are produced are generally olefins. These C_4 olefins must be the products of cracking larger hydrocarbons. With only the small yields of C_3 and C_4 hydrocarbons, the yield of gasoline is quite good with better than 80% of the hydrocarbon products boiling in that range. As will be discussed in the next section, UCC-108 has a significantly better selectivity to gasoline range products. The gasoline produced by ZSM-5 under these conditions should not be aromatic since so little propane and butane is produced. These light paraffins are the usual byproducts of aromatics production. The liquid's refractive index substantiates this hypothesis, indicating the liquid is predominantly olefinic.

The simulated distillations of selected samples from both runs are shown in Figures 7 to 10. As can be readily seen from these distillations, the liquid product boils throughout the gasoline range with some of the product boiling in the diesel range. The products are presumably various branched olefins which should give the gasoline a high research octane number.

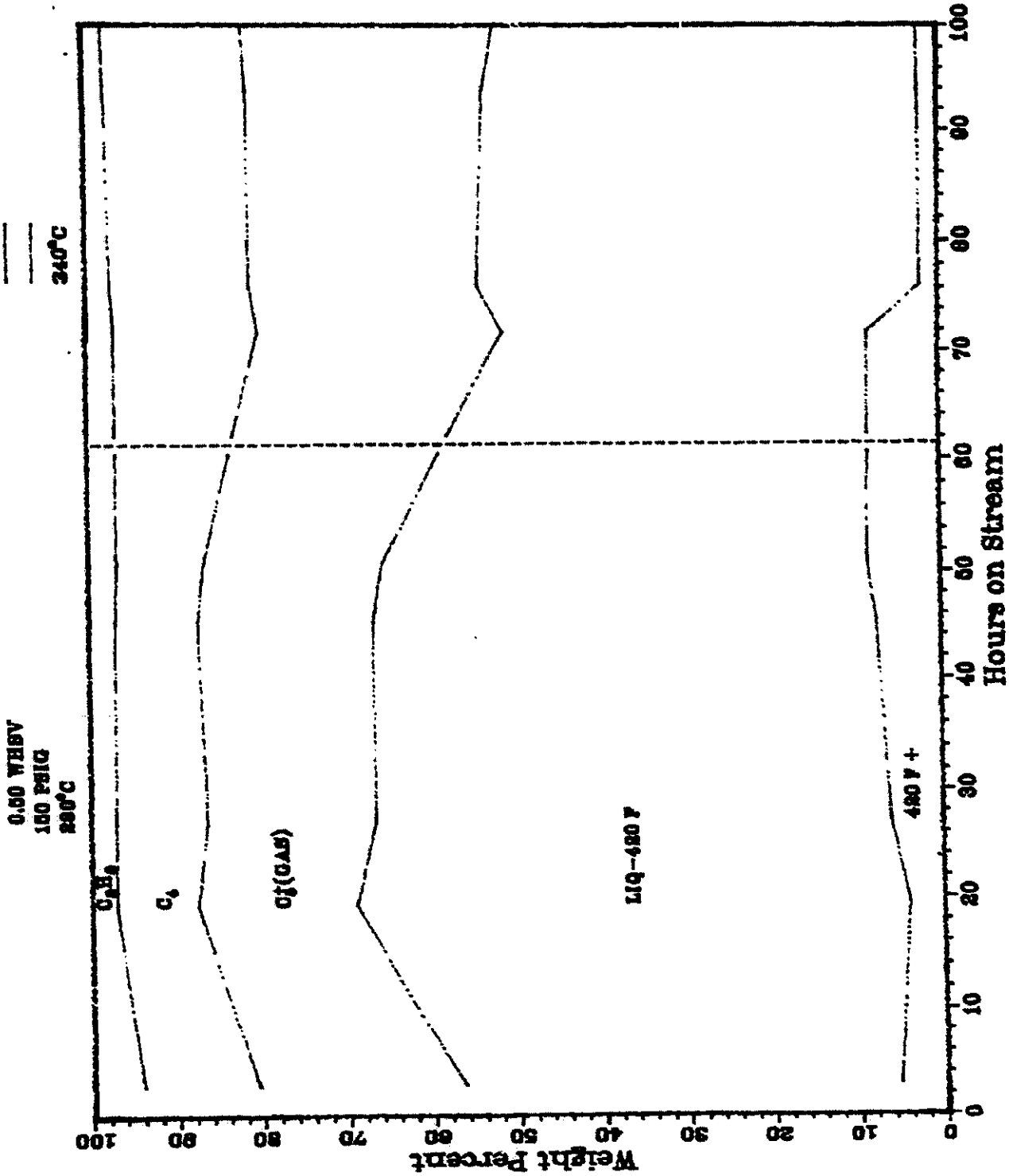
There is little difference in the product selectivities of the two ZSM-5's and the LZ-105-6. The largest difference is in the conversion of the propylene which decreases with increasing silica/alumina ratio. ZSM-5 is an excellent catalyst for propylene oligomerization. (As will be seen in the next section, UCC-108 is even better.)

FIGURE 1



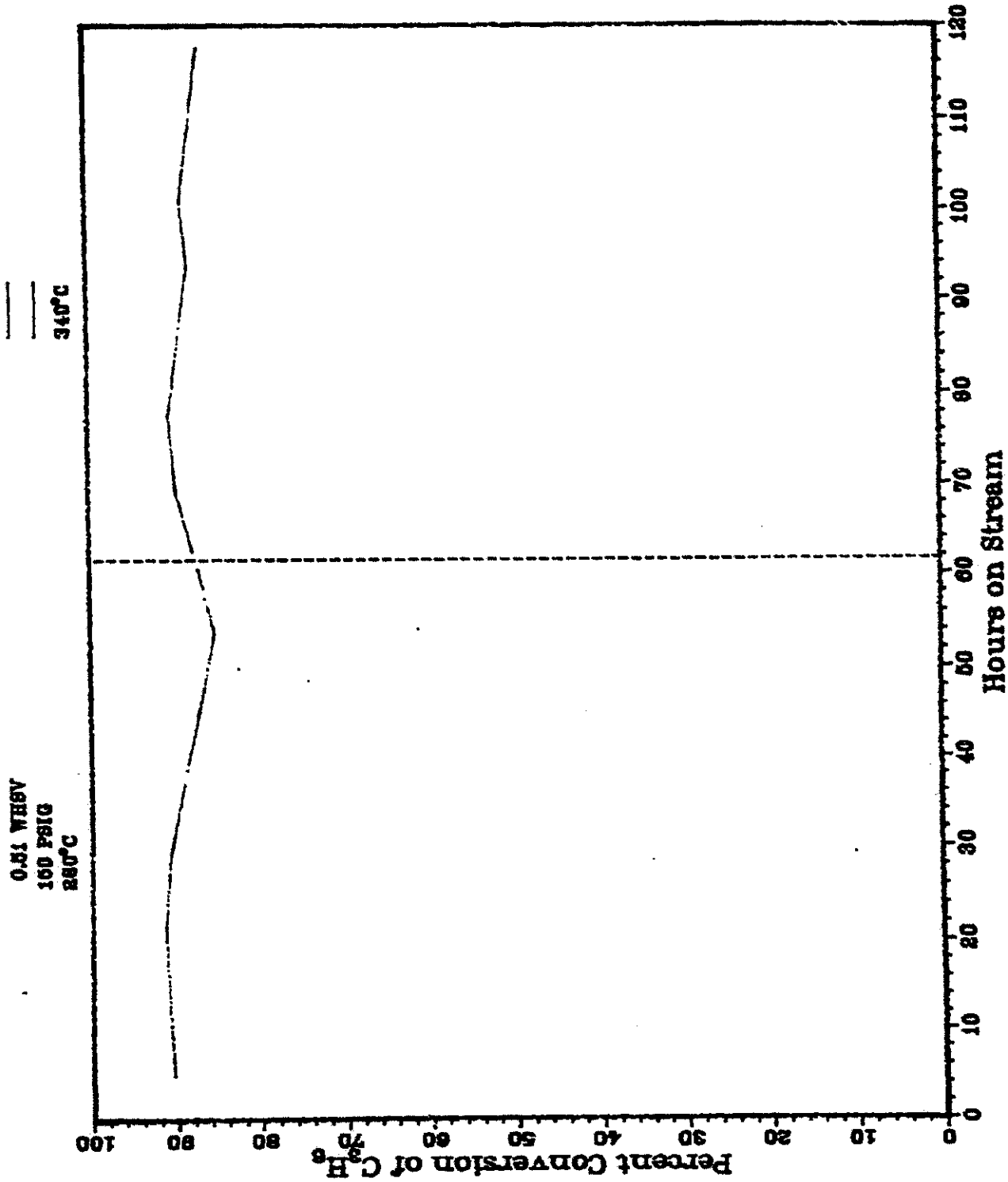
997218

FIGURE 2



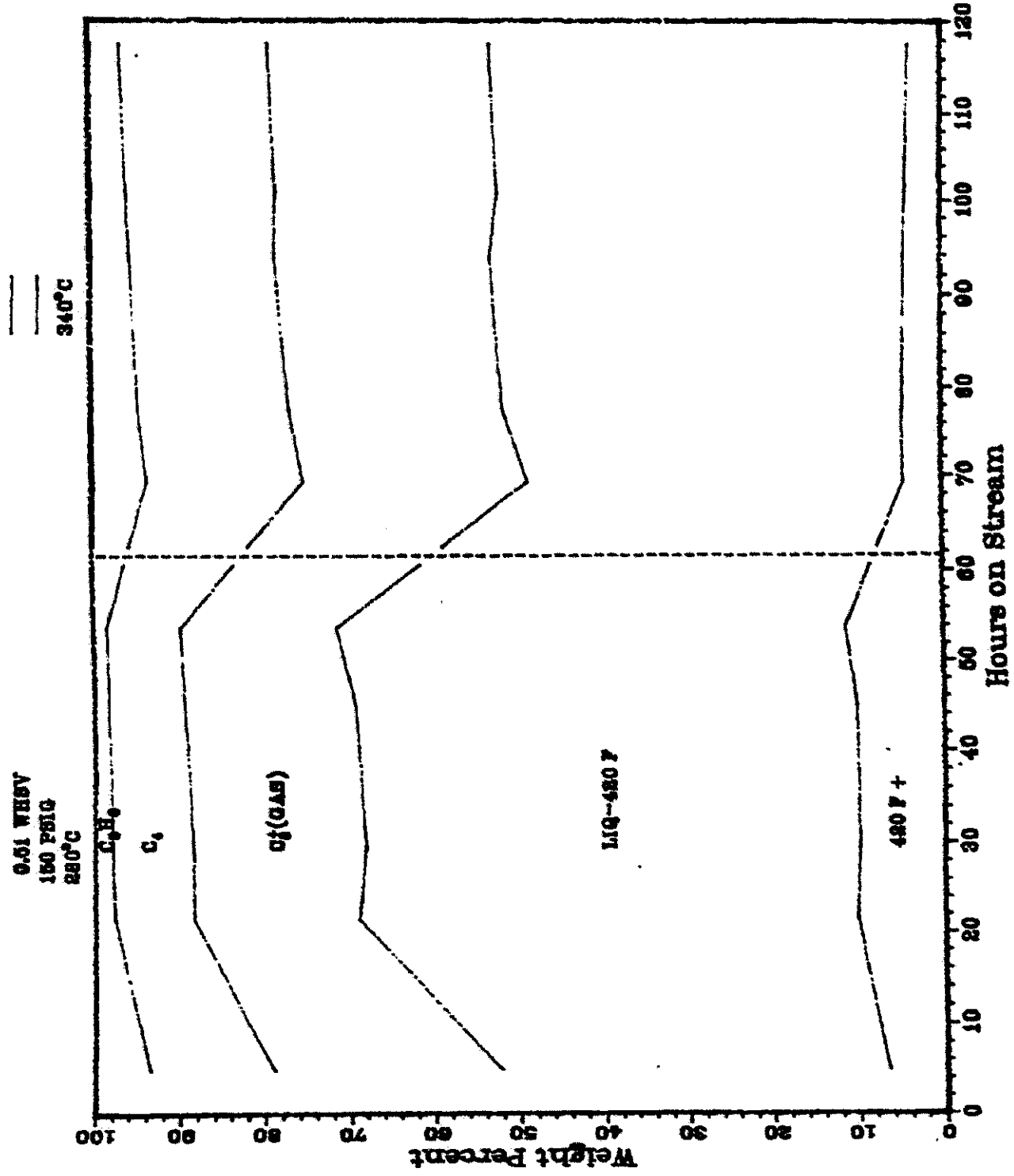
997218

FIGURE 3



997220

FIGURE 4



997220

FIGURE 5

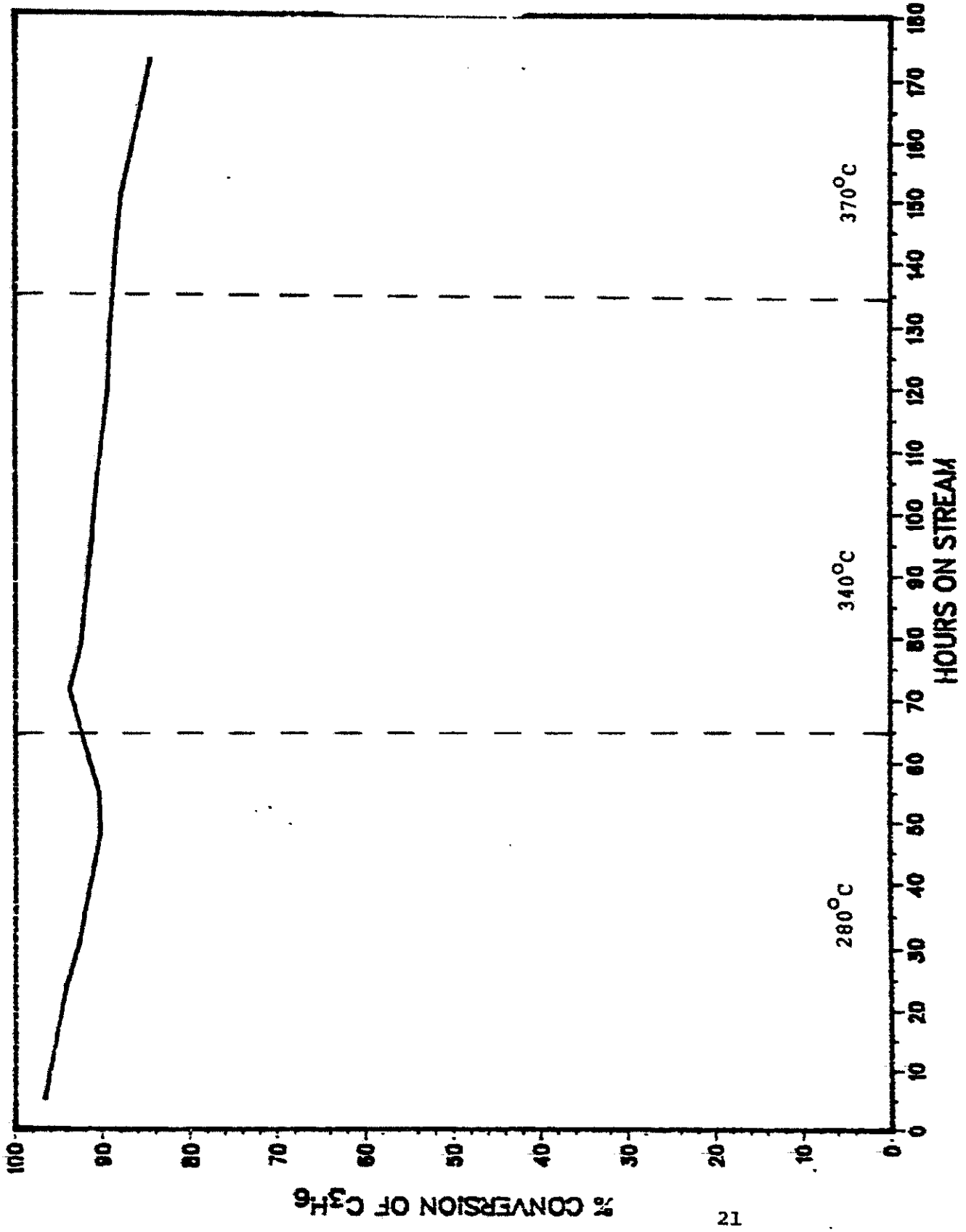

RUN NO. 99/2-15
% CONVERSION OF C_3H_6
HOURS ON STREAM
280°C
340°C
370°C
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

FIGURE 6

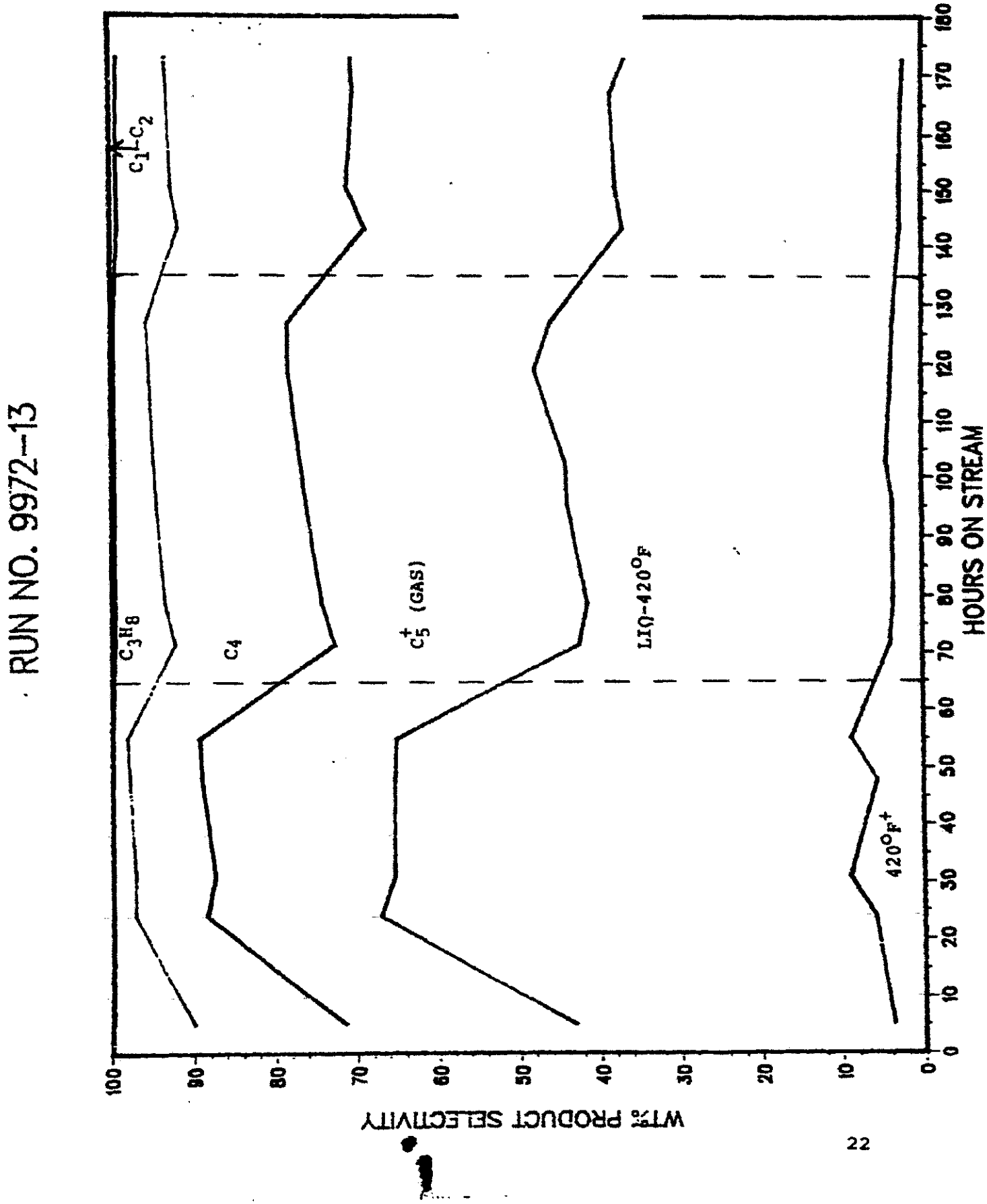

RUN NO. 9972-13
WT% PRODUCT SELECTIVITY
HOURS ON STREAM
C_1-C_2
C_3H_8
C_4
C_5^+ (GAS)
LIQ-420°F
420°F+
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180

FIGURE 7

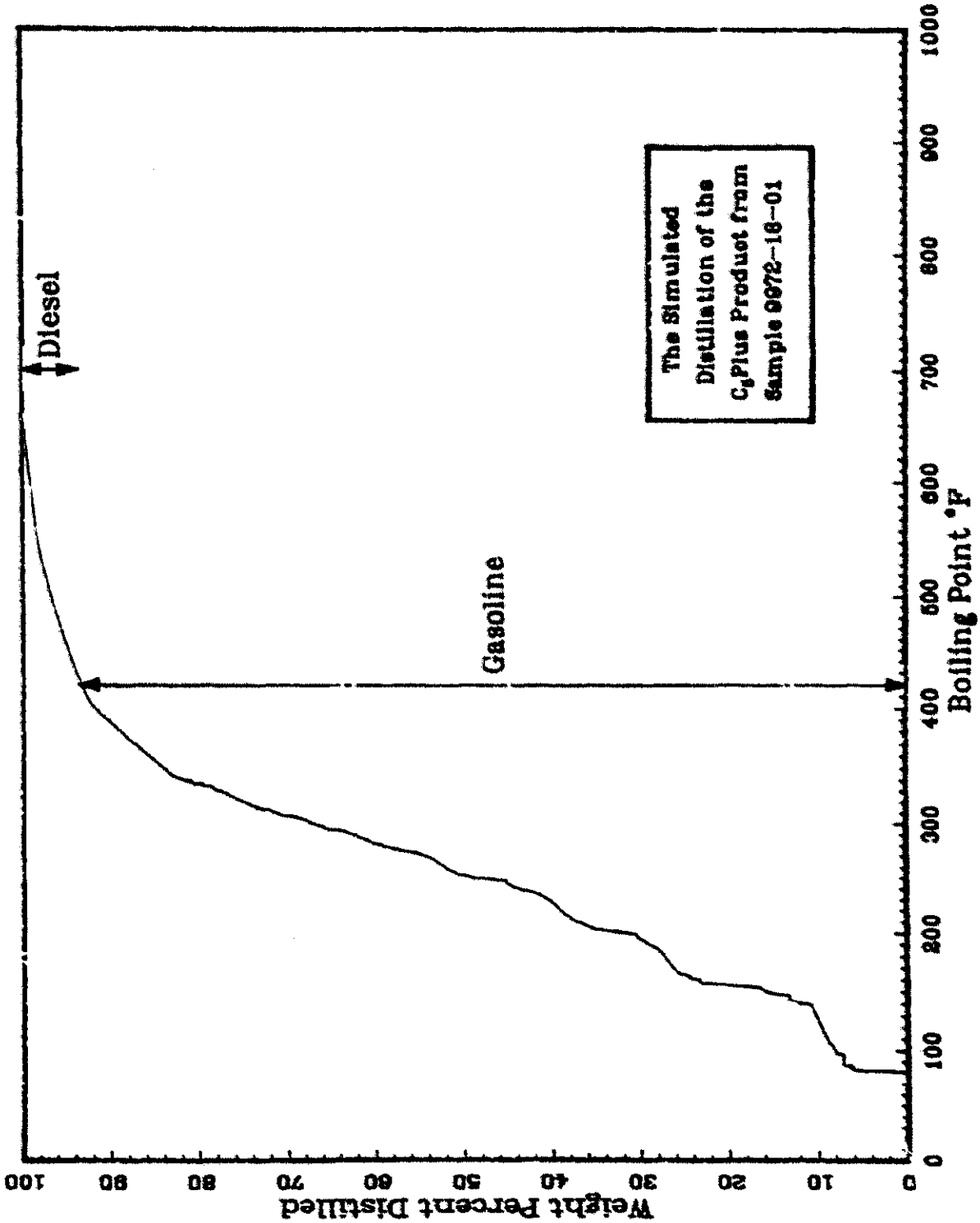

The Simulated Distillation of the C5Plus Product from Sample 9972-18-01
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

FIGURE 8

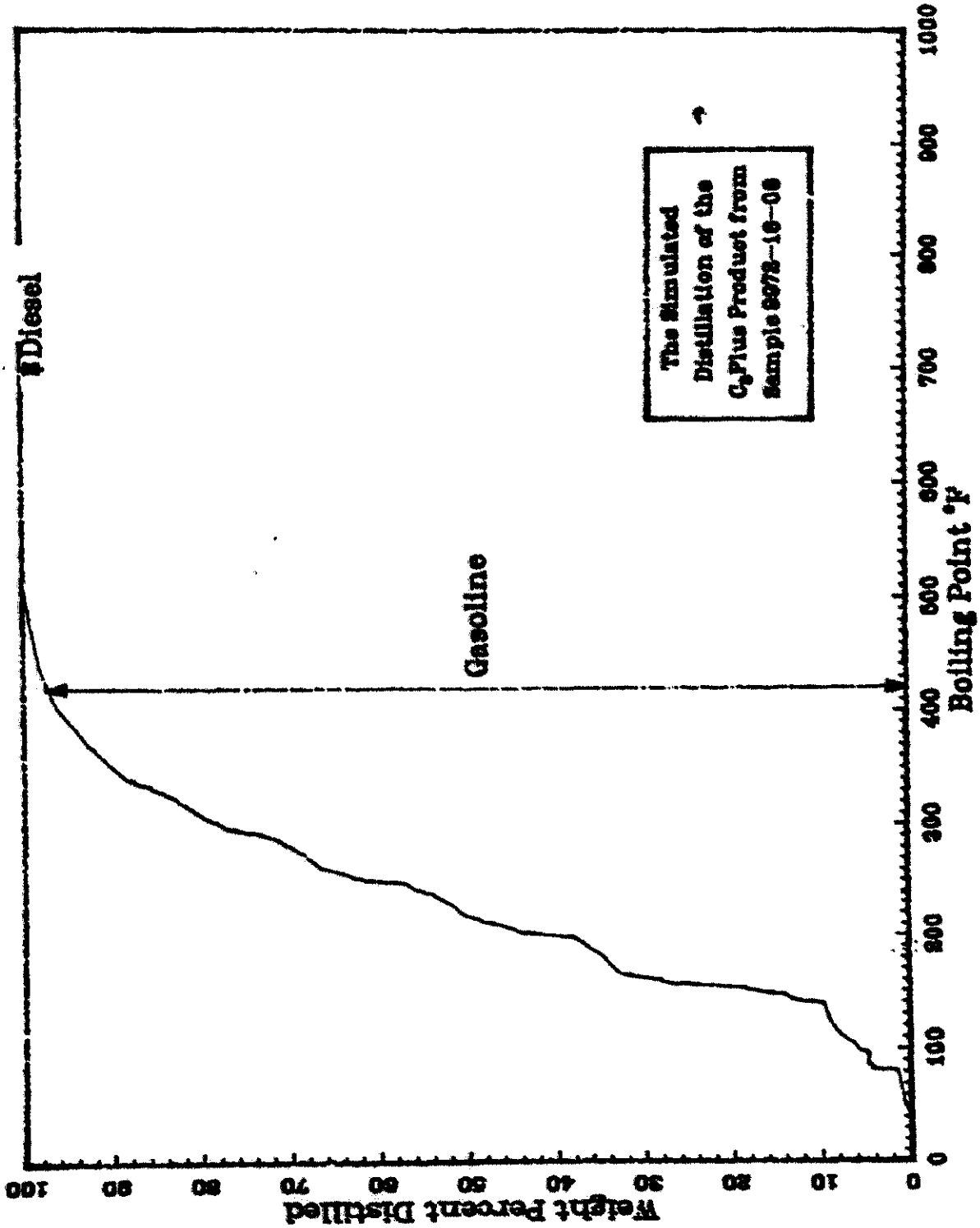

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 8978-10-08
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

FIGURE 9

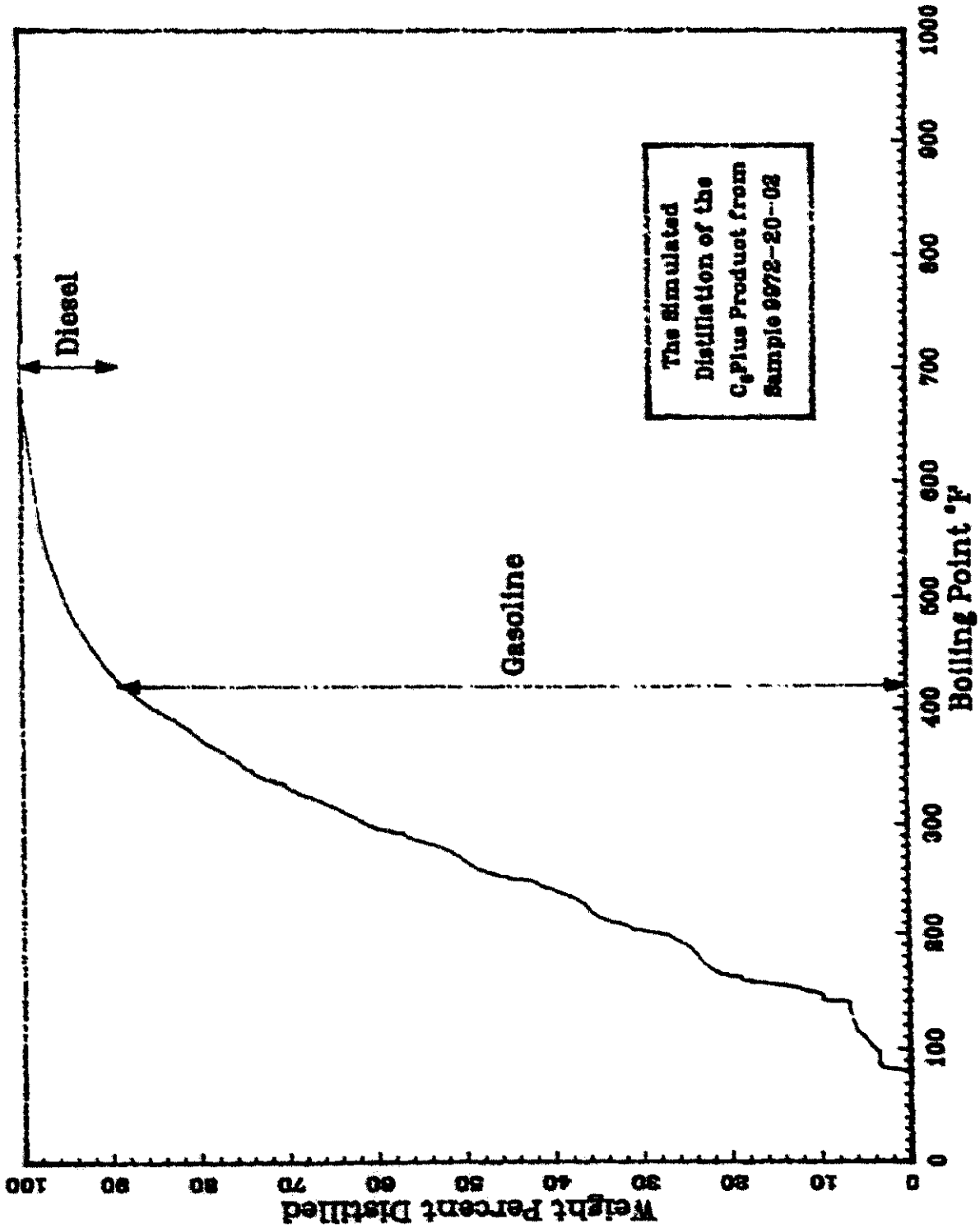

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 9972-20-02
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

FIGURE 10

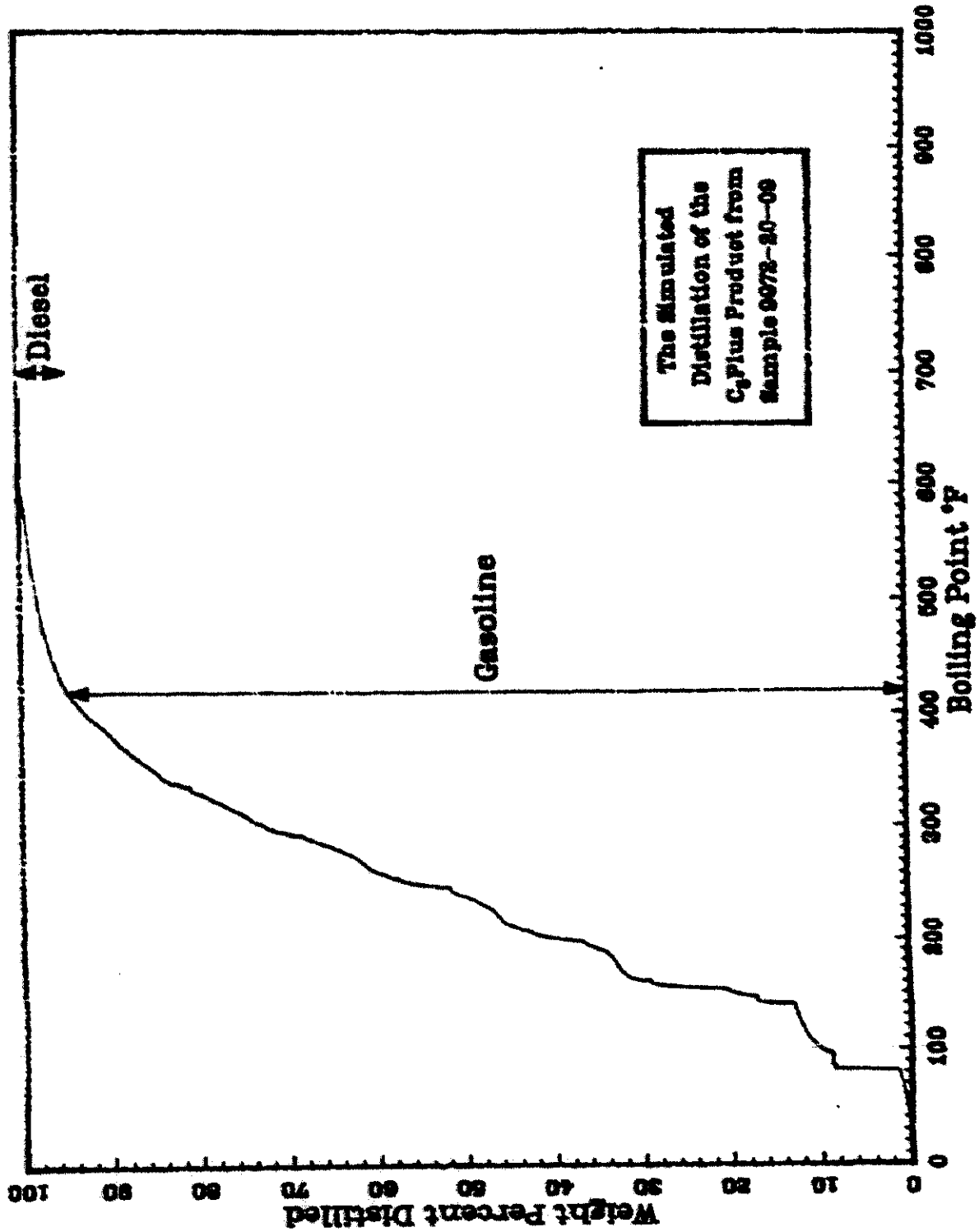

Diesel
Gasoline
The Simulated Distillation of the C5 Plus Product from Sample 00/2-20-09
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
80
90
100

TABLE 1A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-18
CATALYST ZSM-5 #9939-44 54CC 35.00GM (35.59GM AFTER THE RUN, +0.59G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 34.1 CC/HR EFFLUENT 13.1 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-18-01	972-18-02	972-18-03	972-18-04	972-18-05
C3H6 WHSV	0.49	0.51	0.49	0.50	0.51
HRS ON STREAM	2.9	19.5	27.15	45.4	50.9
PRESSURE,PSIG	152	152	154	135	146
TEMP. C	279	279	279	279	279
FEED C3H6 CC	96.91	565.07	270.58	633.03	191.29
HOURS FEEDING	2.90	16.25	8.00	18.25	5.50
EFFLNT GAS LITER	36.40	203.83	107.45	265.55	82.92
GM AQUEOUS LAYER	38.19	234.56	115.74	242.38	74.26
GM LIQ HYDROCARBON	20.26	133.24	56.24	104.45	26.30
WT FR. LIQ HC/FEED	0.4110	0.4635	0.4086	0.3244	0.2703
MATERIAL BALANCE WT %	92.97	92.42	95.97	97.70	97.94
C3H6 CONVERSION %	84.43	73.75	65.72	50.34	43.70
PRDT SELECTIVITY,WT %					
CH4	0.00	0.00	0.00	0.00	0.00
C2 HC'S	0.10	0.05	0.03	0.00	0.02
C3H8	5.74	2.90	3.05	3.13	3.34
C4H10	6.97	2.06	2.01	1.46	1.39
C4H8=	6.59	7.48	8.61	8.17	8.74
C5H12	5.59	1.75	1.49	1.13	0.99
C5H10=	0.24	0.36	0.42	0.44	0.50
C6H14	7.15	4.67	4.04	3.61	3.39
C6H12= & CYCLO'S	2.54	3.15	4.09	4.23	4.41
C7+ IN GAS	8.58	8.77	9.74	11.29	11.74
LIQ HC'S	56.51	68.84	66.52	66.55	65.47
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	19.40	12.47	13.70	12.76	13.50
C5 -420 F	75.24	83.46	80.18	79.65	77.99
420-700 F	5.37	4.06	6.12	7.59	8.51
700-END PT	0.00	0.00	0.00	0.00	0.00
C5+-END PT	80.60	87.53	86.30	87.24	86.50
ISO/NORMAL MOLE RATIO					
C4	1.5218	1.2047	1.0059	0.9882	1.0146
C5	1.7258	1.3639	1.3957	1.2251	1.1840
C6	8.2157	11.2969	11.7850	10.1468	10.7688
C4=	0.3678	0.1978	0.1615	0.1359	0.1276

PARAFFIN/OLEFIN RATIO					
C3	0.2995	0.0779	0.0560	0.0304	0.0248
C4	1.0220	0.2656	0.2259	0.1727	0.1538
C5	22.7112	4.7759	3.4449	2.4776	1.9374
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLEAR OIL	CLEAR OIL	CLEAR OIL	CLEAR OIL	CLEAR OIL
DENSITY	0.759	0.748	0.748	0.750	0.751
N. REFRACTIVE INDEX	1.4363	1.4285	1.4275	1.4275	1.4283
SIMULT'D DISTILATN					
10 WT % @ DEG F	170	154	184	200	209
16	197	170	210	221	234
50	288	261	295	307	312
84	380	358	381	394	402
90	414	390	412	435	450
RANGE(16-84 %)	183	188	171	173	168
WT % @ 420 F	90.5	94.1	90.8	88.6	87.0
WT % @ 700 F	100	100	100	100	100

TABLE 1B RESULT OF PROPYLENE OPERATION

RUN NO. 9972-18
CATALYST ZSM-5 #9939-44 54CC 35.00GM (35.59GM AFTER THE RUN, +0.59G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 34.1 CC/HR EFFLUENT 13.1 L/HR AQ LAYR 13.9 CC/HR

RUN & SAMPLE NO.	9972-18-06	972-18-07	972-18-08	972-18-09
C3H6 WHSV	0.52	0.51	0.51	0.50
HRS ON STREAM	71.82	76.24	93.74	99.91
PRESSURE,PSIG	151	150	147	154
TEMP. C	339	339	340	340
FEED C3H6 CC	675.82	154.80	610.38	213.95
HOURS FEEDING	18.92	4.42	17.50	6.17
EFFLNT GAS LITER	246.49	55.90	227.65	78.55
GM AQUEOUS LAYER	272.51	64.30	252.84	89.31
GM LIQ HYDROCARBON	137.79	32.94	131.34	45.79
WT FR. LIQ HC/FEED	0.4008	0.4183	0.4230	0.4207
MATERIAL BALANCE WT %	93.78	96.11	92.73	97.41
C3H6 CONVERSION %	84.45	84.03	86.43	85.64
PRDT SELECTIVITY,WT %				
CH4	0.01	0.02	0.02	0.02
C2 HC'S	0.30	0.27	0.21	0.18
C3H8	3.08	2.64	2.21	2.05
C4H10	3.89	3.02	2.16	2.06
C4H8=	13.04	13.32	14.49	14.31
C5H12	3.94	3.16	2.47	2.53
C5H10=	0.42	0.43	0.46	0.51
C6H14	9.97	9.17	9.56	10.03
C6H12= & CYCLO'S	4.24	4.26	4.64	5.33
C7+ IN GAS	10.04	9.65	10.46	10.96
LIQ HC'S	51.06	54.06	53.31	52.03
TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	20.32	19.26	19.09	18.61
C5 -420 F	71.40	78.63	78.61	79.05
420-700 F	8.27	2.11	2.29	2.34
700-END PT	0.00	0.00	0.00	0.00
C5+-END PT	79.68	80.74	80.91	81.39
ISO/NORMAL MOLE RATIO				
C4	2.1699	2.3078	2.3233	2.1780
C5	2.0037	1.8915	1.7441	1.6120
C6	12.6516	14.0644	15.4883	15.3583
C4=	0.4502	0.4377	0.4248	0.4071

PARAFFIN/OLEFIN RATIO				
C3	0.1606	0.1333	0.1350	0.1172
C4	0.2878	0.2187	0.1442	0.1388
C5	9.0552	7.2249	5.1665	4.8597
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLEAR OIL	CLEAR OIL	CLEAR OIL	CLEAR OIL
DENSITY	0.754	0.744	0.739	0.738
N, REFRACTIVE INDEX	1.4312	1.4263	1.4228	1.4236
SIMULT'D DISTILATN				
10 WT % @ DEG F	212	147	145	149
16	238	167	164	165
50	319	261	256	256
84	420	343	349	349
90	474	371	379	379
RANGE(16-84 %)	182	176	185	184
WT % @ 420 F	83.8	96.1	95.7	95.5
WT % @ 700 F	100	100	100	100

TABLE 2A RESULT OF PROPYLENE OPERATION

RUN NO. 9972-20
CATALYST H-ZSM-5 #10042-65 59 CC 35.0 GM (40.1 AFTER RUN +5.1G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 35.5 CC/HR EFFLUENT 13.1 L/HR AQ LAYR 14.5 CC/HR

RUN & SAMPLE NO.	9972-20-01	972-20-02	972-20-03	972-20-04	972-20-05
C3H6 WHSV	0.51	0.52	0.50	0.52	0.51
HRS ON STREAM	4.83	21.41	29.41	44.91	53.83
PRESSURE,PSIG	145	146	143	151	151
TEMP. C	279	278	279	278	278
FEED C3H6 CC	169.27	592.88	276.12	560.04	310.22
HOURS FEEDING	4.83	16.58	8.00	15.50	8.92
EFFLNT GAS LITER	62.99	204.10	104.26	198.00	112.97
GM AQUEOUS LAYER	66.19	239.19	115.24	223.35	127.32
GM LIQ HYDROCARBON	35.18	172.28	83.06	160.71	91.10
WT FR. LIQ HC/FEED	0.4086	0.5712	0.5913	0.5641	0.5773
MATERIAL BALANCE WT %	90.21	91.70	98.20	94.42	96.97
C3H6 CONVERSION %	90.53	91.38	90.69	87.33	85.34
PRDT SELECTIVITY,WT %					
CH4	0.01	0.01	0.01	0.00	0.01
C2 HC'S	0.10	0.06	0.06	0.04	0.04
C3H8	6.37	2.32	2.08	1.75	1.63
C4H10	8.57	2.01	1.65	1.02	0.80
C4H8=	5.93	7.25	7.80	7.88	7.88
C5H12	7.86	2.19	1.88	1.35	1.09
C5H10=	0.19	0.25	0.28	0.30	0.30
C6H14	8.53	6.60	6.65	6.63	5.79
C6H12= & CYCLO'S	2.07	2.97	3.23	3.46	3.20
C7+ IN GAS	8.20	7.35	8.25	8.26	7.86
LIQ HC'S	52.17	68.99	68.09	69.31	71.42
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	20.98	11.65	11.61	10.69	10.35
C5 -420 F	72.39	78.14	78.45	79.05	78.22
420-700 F	6.63	10.21	9.94	10.26	11.43
700-END PT	0.00	0.00	0.00	0.00	0.00
C5+-END PT	79.02	88.35	88.39	89.31	89.65
ISO/NORMAL MOLE RATIO					
C4	1.5548	1.8799	1.9144	1.8711	1.9078
C5	1.8088	1.7077	1.6529	1.4472	1.4069
C6	6.7192	13.4260	14.7159	16.0544	17.0921
C4=	0.4713	0.4230	0.3952	0.3713	0.3439

PARAFFIN/OLEFIN RATIO					
C3	0.5871	0.2354	0.1943	0.1154	0.0906
C4	1.3955	0.2679	0.2045	0.1245	0.0977
C5	39.3409	8.3855	6.4657	4.3639	3.5651
LIQ HC COLLECTION					
PHYS. APPEARANCE	GRN OIL	GRN OIL	GRN OIL	GRN OIL	GRN OIL
DENSITY	0.762	0.742	0.744	0.741	0.740
N, REFRACTIVE INDEX	1.4409	1.4303	1.4295	1.4260	1.4234
SIMULT'D DISTILATN					
10 WT % @ DEG F	160	164	166	170	170
16	193	194	197	202	204
50	293	297	298	300	303
84	403	414	413	413	420
90	441	456	454	454	464
RANGE(16-84 %)	210	220	216	211	216
WT % @ 420 F	87.3	85.2	85.4	85.2	84.0
WT % @ 700 F	100.0	100.0	100.0	100.0	100.0

TABLE 28 RESULT OF PROPYLENE OPERATION

RUN NO. 9972-20
CATALYST H-ZSM-5 #10042-65 59 CC 35.0 GM (40.1 AFTER RUN +5.1G)
FEED H2:C3H6:H2O @ 1:1:2 MOLE RATIO,0.5 C3H6 WHSV,CONTINUOUS FEED
C3H6 MW= 42.0813 DENSITY= 0.5087 GM/CC (@ 73 F)
TARGET FLOW: C3H6 34.3 CC/HR H2 168 CCMN,10.1 L/HR H2O 15.0 CC/HR
ACTUAL FLOW: 35.5 CC/HR EFFLUENT 13.1 L/HR AQ LAYR 14.5 CC/HR

RUN & SAMPLE NO.	9972-20-06	972-20-07	972-20-08	972-20-09	972-20-10
C3H6 WHSV	0.51	0.50	0.53	0.49	0.52
HRS ON STREAM	69.25	77.5	93.67	100.84	117.59
PRESSURE,PSIG	149	147	145	154	147
TEMP. C	336	337	337	337	337
FEED C3H6 CC	540.49	284.42	591.50	244.15	600.94
HOURS FEEDING	15.42	8.25	16.17	7.17	16.75
EFFLNT GAS LITER	209.48	109.30	218.58	95.48	227.32
GM AQUEOUS LAYER	226.60	118.84	237.27	104.40	244.47
GM LIQ HYDROCARBON	122.48	66.75	132.45	58.50	134.45
WT FR. LIQ HC/FEED	0.4455	0.4613	0.4402	0.4710	0.4398
MATERIAL BALANCE WT %	103.07	101.19	95.47	104.92	96.90
C3H6 CONVERSION %	89.69	90.41	88.11	88.85	86.64
PRDT SELECTIVITY,WT %					
CH4	0.03	0.03	0.03	0.02	0.02
C2 HC'S	0.38	0.40	0.40	0.36	0.35
C3H8	6.26	5.36	4.36	4.09	3.47
C4H10	11.15	9.39	7.29	6.83	5.39
C4H8=	7.16	8.22	9.71	10.69	11.96
C5H12	9.75	8.17	6.62	6.14	5.10
C5H10=	0.24	0.27	0.29	0.32	0.35
C6H14	7.71	7.80	8.33	8.69	9.00
C6H12= & CYCLO'S	1.47	1.84	2.31	2.69	3.01
C7+ IN GAS	7.12	6.96	7.79	8.25	8.45
LIQ HC'S	48.72	51.55	52.86	51.90	52.91
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	24.99	23.41	21.79	22.00	21.19
C5 -420 F	70.58	72.11	73.92	73.84	75.06
420-700 F	4.43	4.48	4.28	4.15	3.76
700-END PT	0.00	0.00	0.00	0.00	0.00
C5+-END PT	75.01	76.59	78.21	78.00	78.81
ISO/NORMAL MOLE RATIO					
C4	2.2268	2.3590	2.5016	2.4977	2.5185
C5	2.6767	2.6384	2.6645	2.6039	2.5002
C6	7.1991	8.0540	9.4070	10.1768	11.3599
C4=	0.4631	0.4695	0.4748	0.4699	0.4630

PARAFFIN/OLEFIN RATIO					
C3	0.5259	0.4865	0.3112	0.3138	0.2163
C4	1.5028	1.1030	0.7249	0.6168	0.4351
C5	40.0225	29.4922	22.4699	18.7759	14.0341
LIQ HC COLLECTION					
PHYS. APPEARANCE	YL-GR OIL	YL-GR OIL	YL-GR OIL	YL-GR OIL	YL-GR OIL
DENSITY	0.766	0.767	0.759	0.760	0.756
N. REFRACTIVE INDEX	1.4394	1.4359	1.4331	1.4306	1.4286
SIMULT'D DISTILATN					
10 WT % @ DEG F	150	149	151	155	151
16	189	186	181	184	172
50	285	283	281	279	273
84	384	381	377	377	370
90	413	411	407	407	401
RANGE(16-84 %)	195	195	196	193	198
WT % @ 420 F	90.9	91.25	91.90	92.00	92.90
WT % @ 700 F	100.0	100.0	100.0	100.0	100.0

UCC-108, Run 9972-22

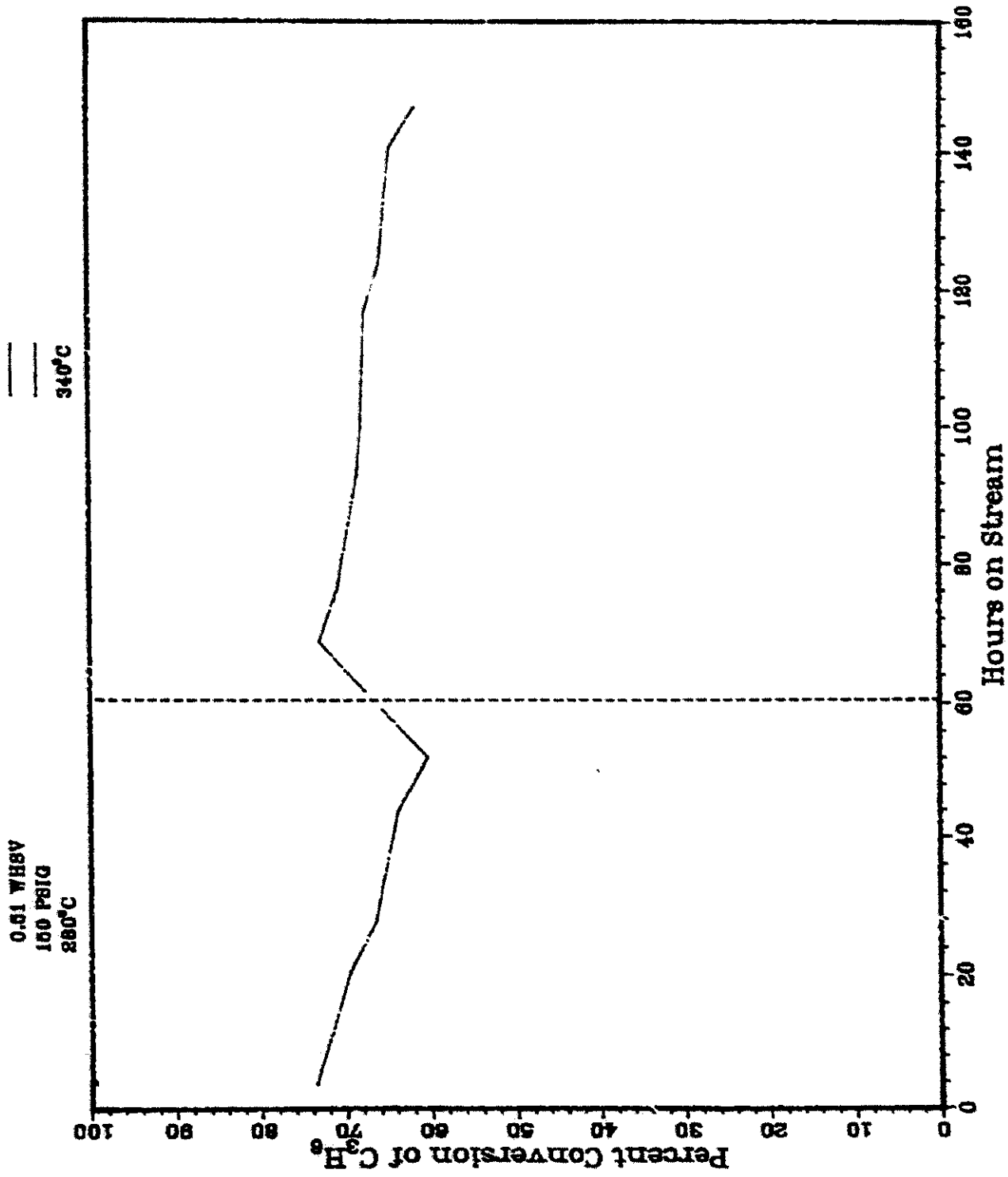
UCC-108 is a new Union Carbide proprietary molecular sieve. It is related to UCC-104 and should be considered a more active modification of UCC-104.

The conversion and product selectivity are shown in Figures 11 and 12. The simulated distillation of selected C_5^+ products are presented in figures 13 to 15. The detailed material balances and selectivities are presented in tables 3A to 3C.

This is an excellent catalyst for the conversion of propylene to gasoline range products. The conversion of propylene is quite high at 280°C. It is 75% higher than was achieved by UCC-104 under comparable conditions. The conversion with UCC-108 is lower than that of LZ-105-6 on ZSM-5 with a silica/alumina ratio of 35 but is higher than the average conversion of the ZSM-5 with a silica alumina ratio of 85. With UCC-108 the conversion did not significantly increase with the temperature increase from 280 to 340°C.

The products of this reaction are almost exclusively gasoline range hydrocarbons as can be seen in figure 12. There is very little propane or butane formation. This fact suggest the liquid product is olefinic and not aromatic. The density and refractive index of the liquid confirm this suggestion. The simulated distillation of the total C_5^+ product (figures 13 to 15) show the major products to be C_6 olefins. These account for over 70% of the total hydrocarbons produced. The C_5^+ products also contain lesser amounts of C_9 and C_{12} products. This production of gasoline shows little sign of deactivation. As can be seen in figure 15, the simulated distillation of the first sample at 280°C is very similar to that of the final sample at 340°C. The only difference is that more C_6 olefin is produced at 340°C. The UCC-108 seems to act primarily as a dimerization catalyst with some trimerization and further oligomerization. The UCC-108 seems to have little cracking or aromatization activity. This liquid product should be an excellent gasoline. The branched olefins should give it a research octane number over 90.

FIGURE 11



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