Fig. 95

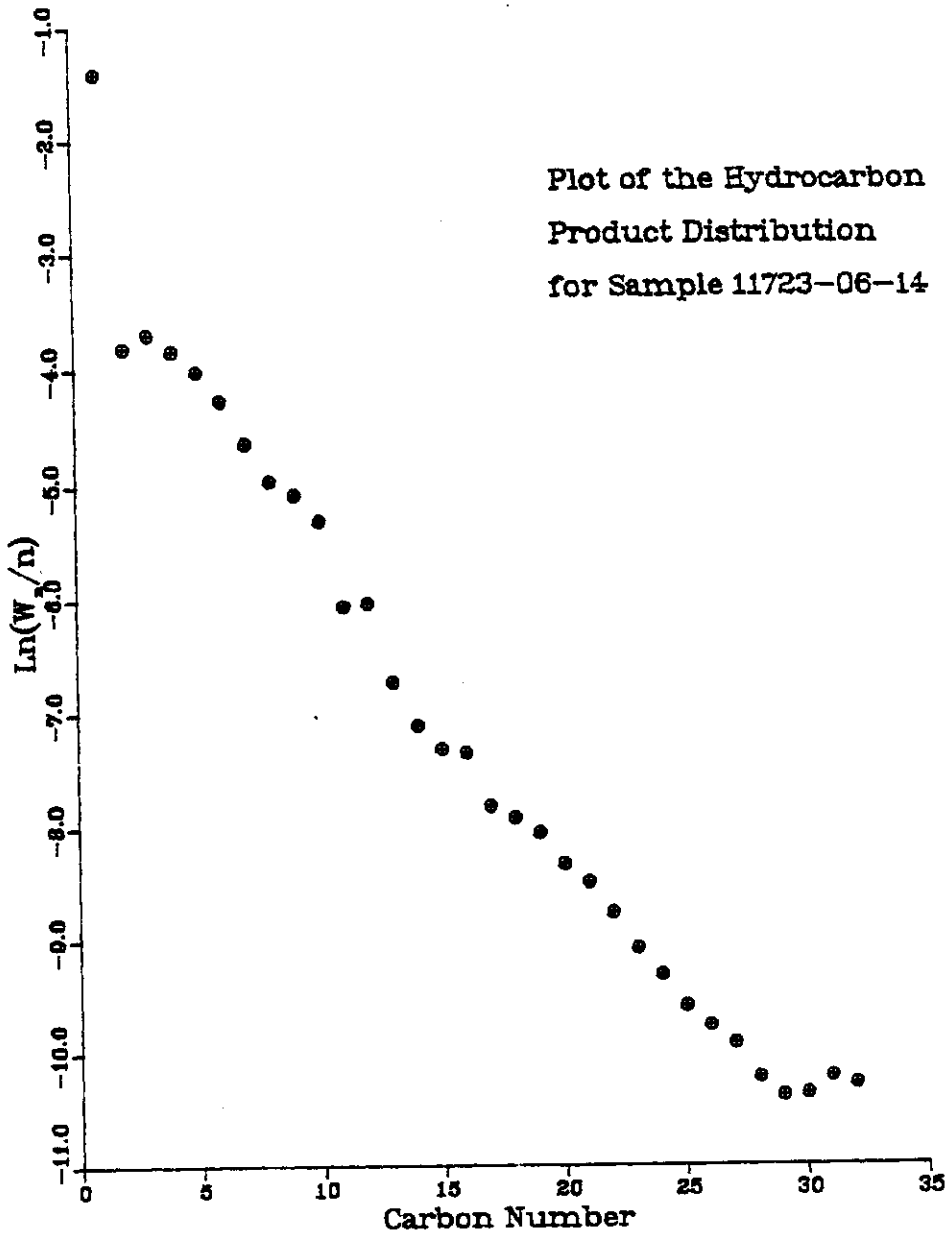
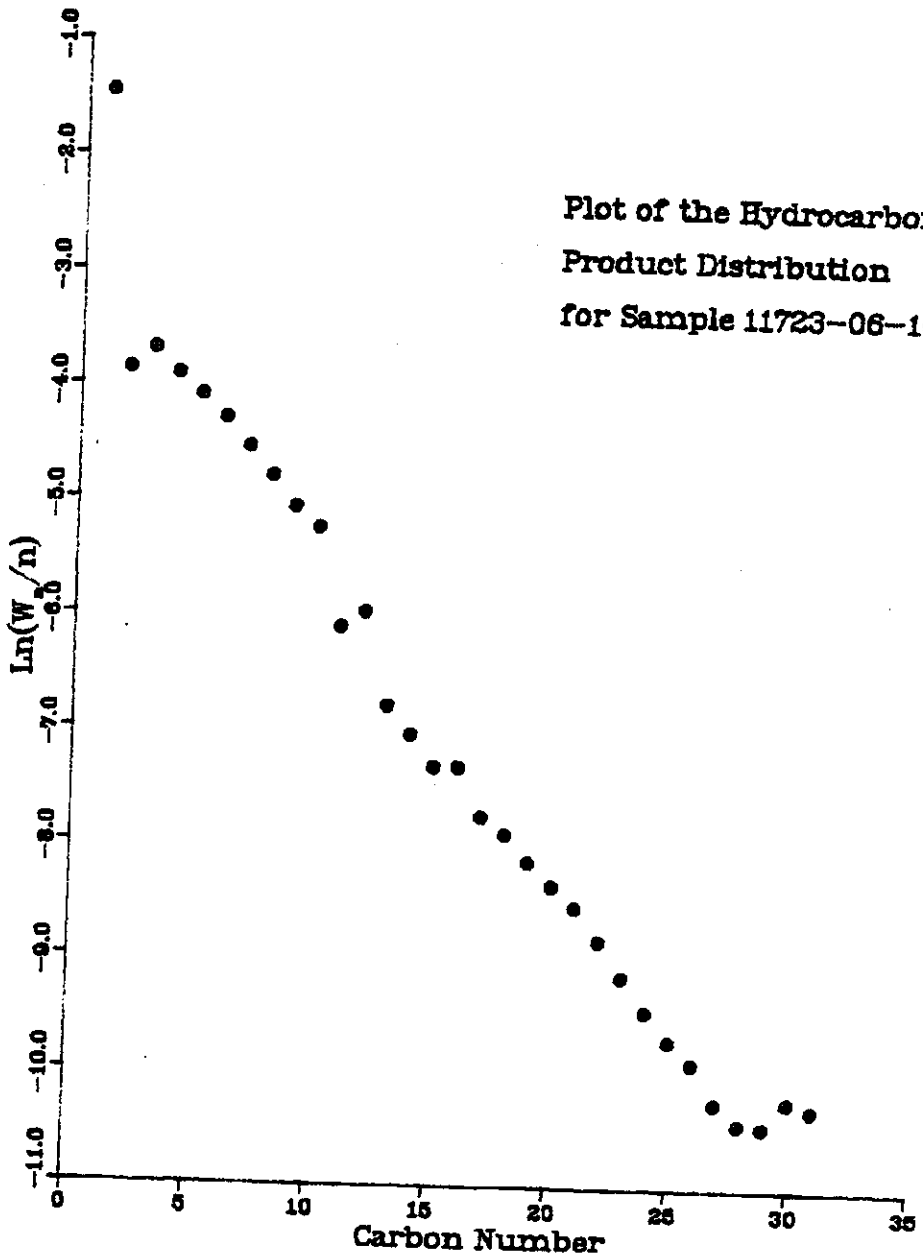
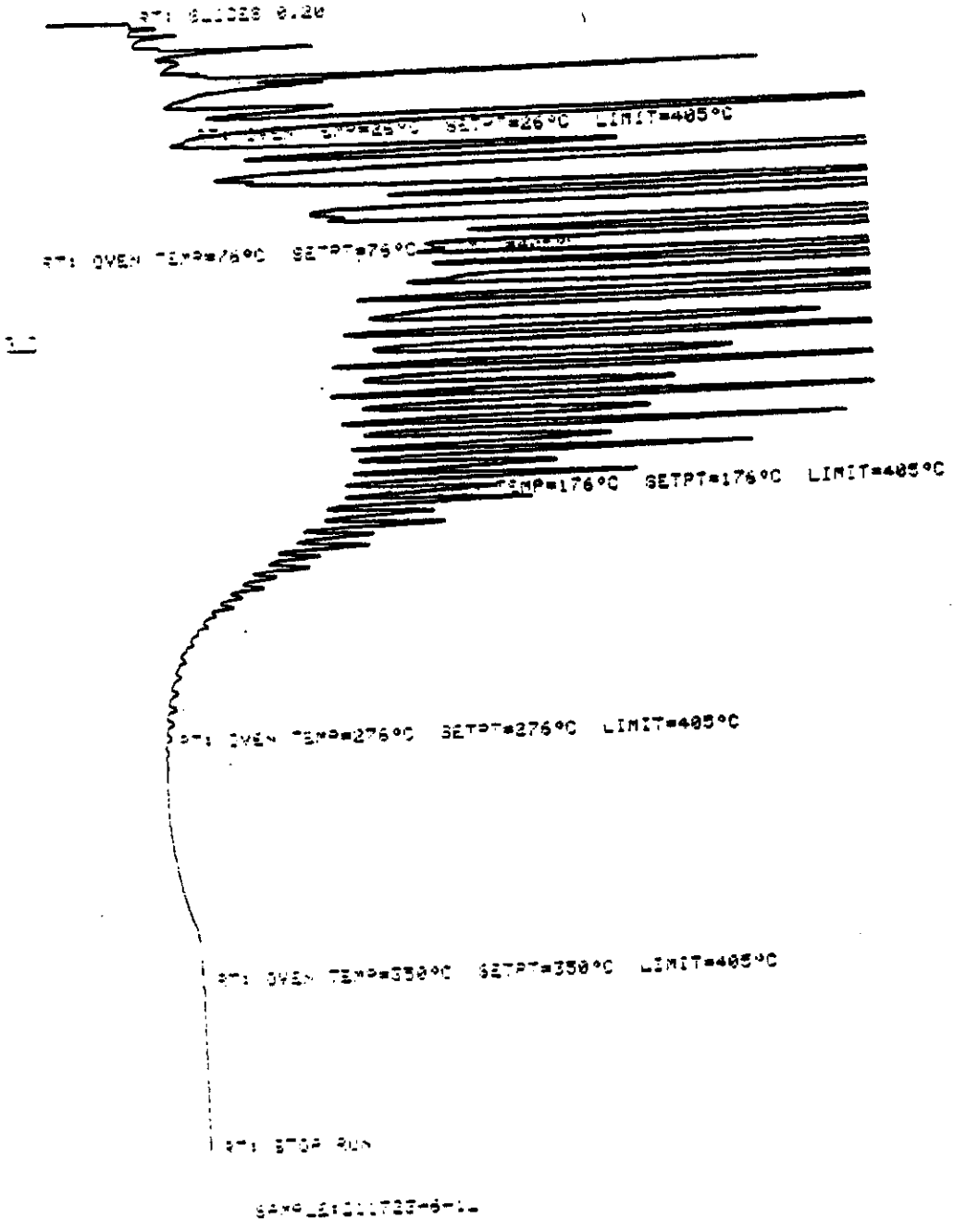

Plot of the Hydrocarbon
Product Distribution
for Sample 11723-06-14
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. 96



Plot of the Hydrocarbon Product Distribution for Sample 11723-06-16

Fig. 97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SETPT=75°C
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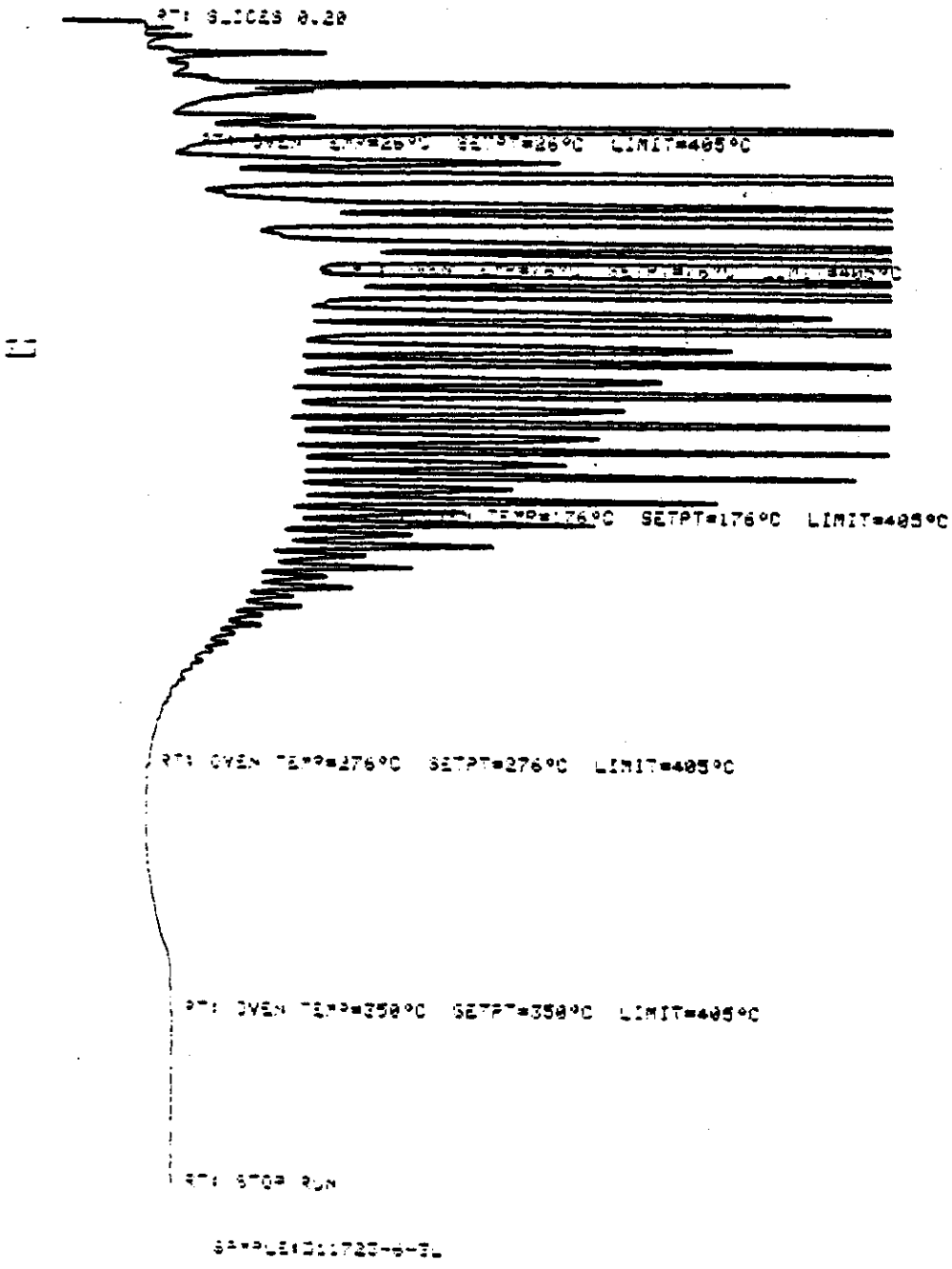
SET TEMP=276°C SETPT=276°C LIMIT=405°C
SET TEMP=350°C SETPT=350°C LIMIT=405°C

Fig. 98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RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 99

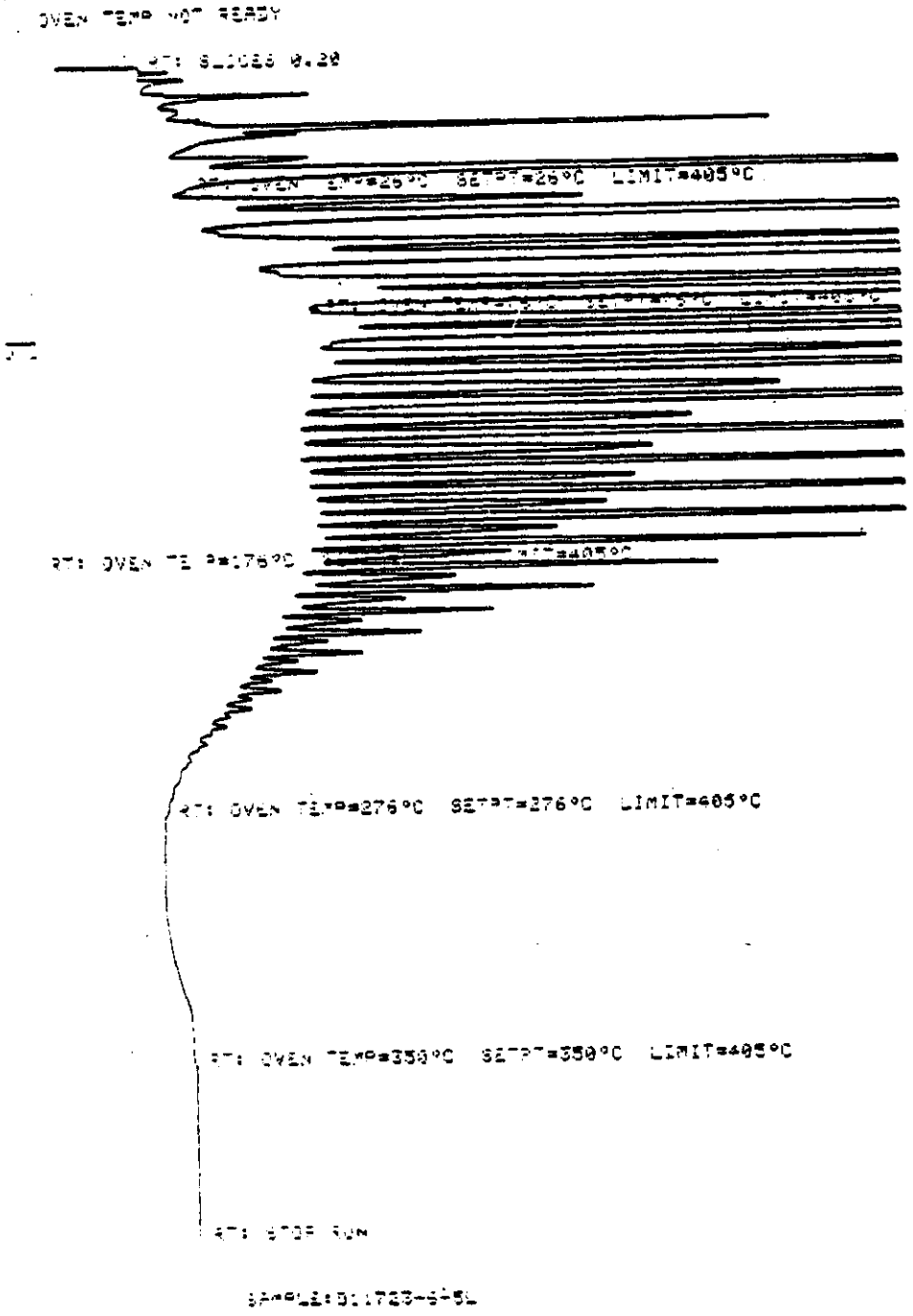
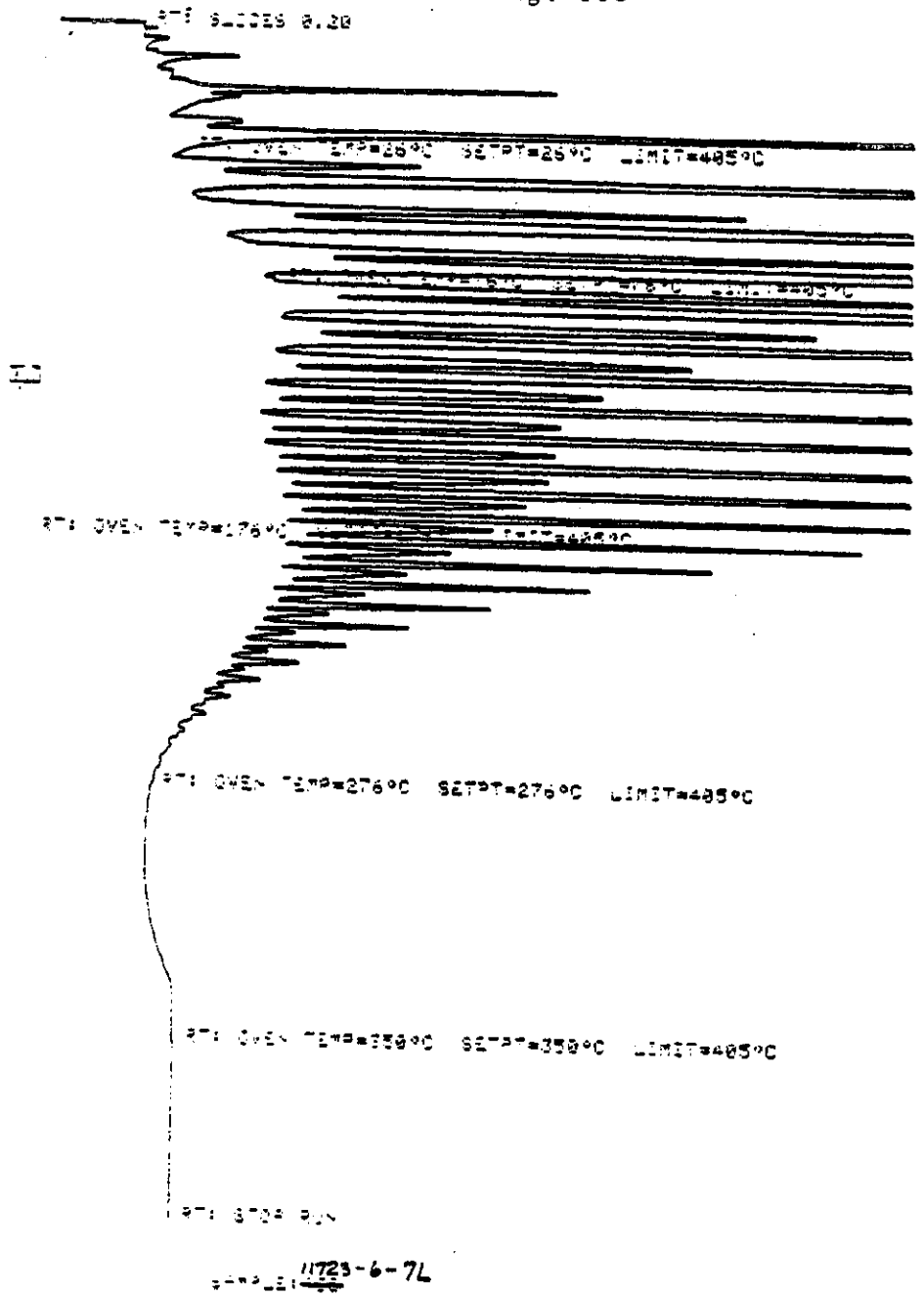

OVEN TEMP NOT READY
RT: OVEN TEMP=25°C SETPT=25°C LIMIT=405°C
RT: OVEN TEMP=175°C
RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C
RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C
RT: STOP RUN

Fig. 100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11723-6-7L

Fig. 101

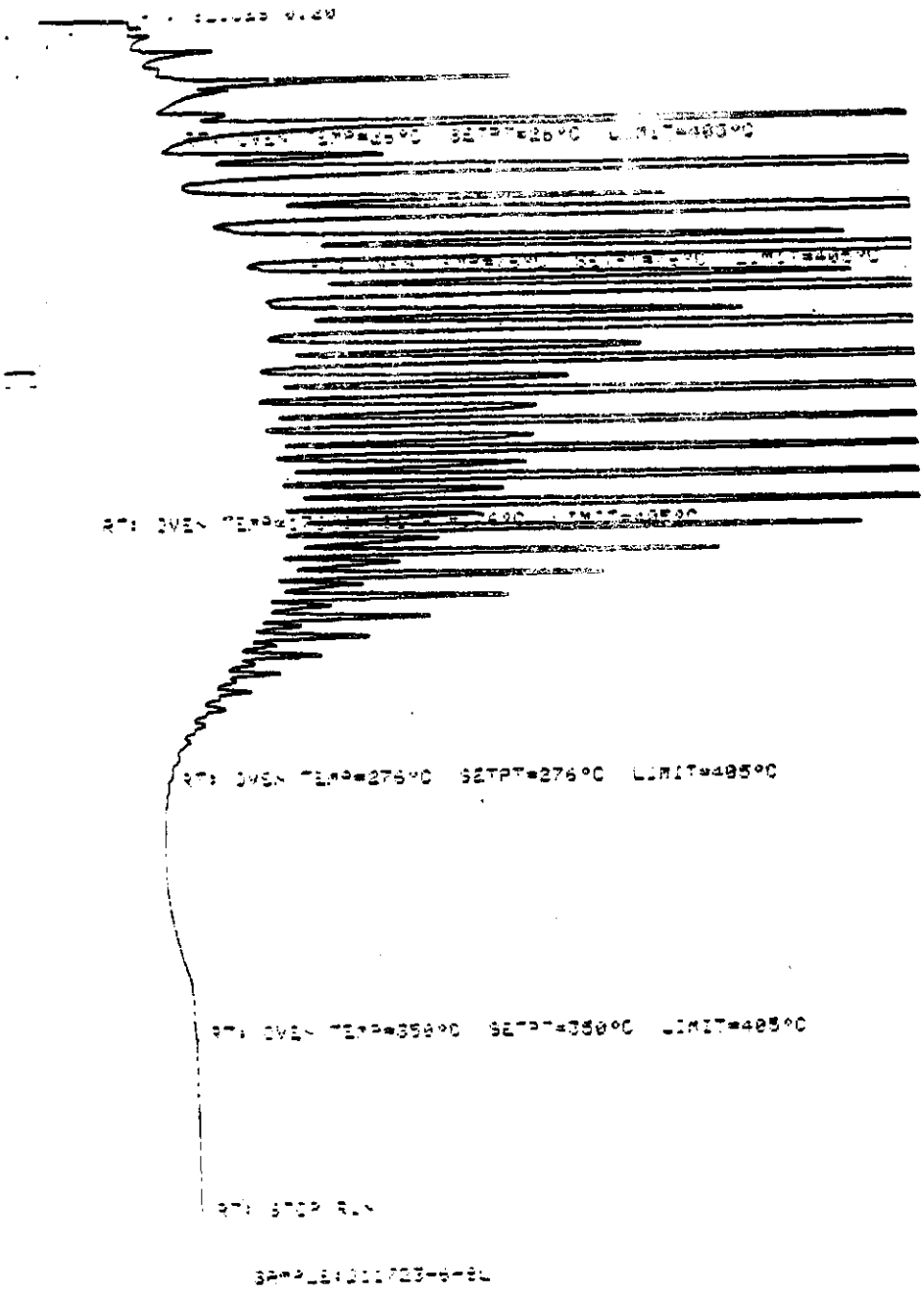

Fig. 102

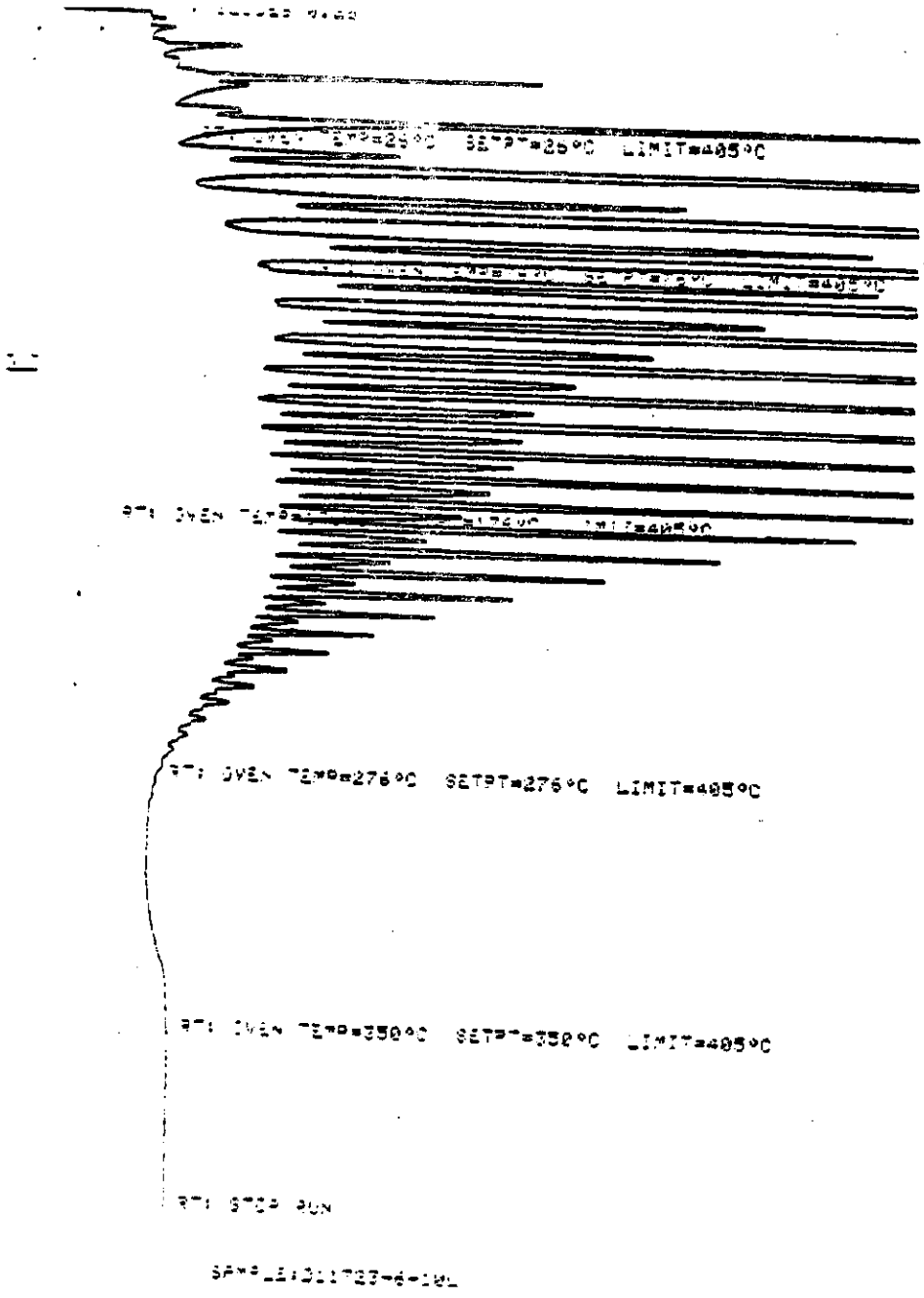

Fig. 103

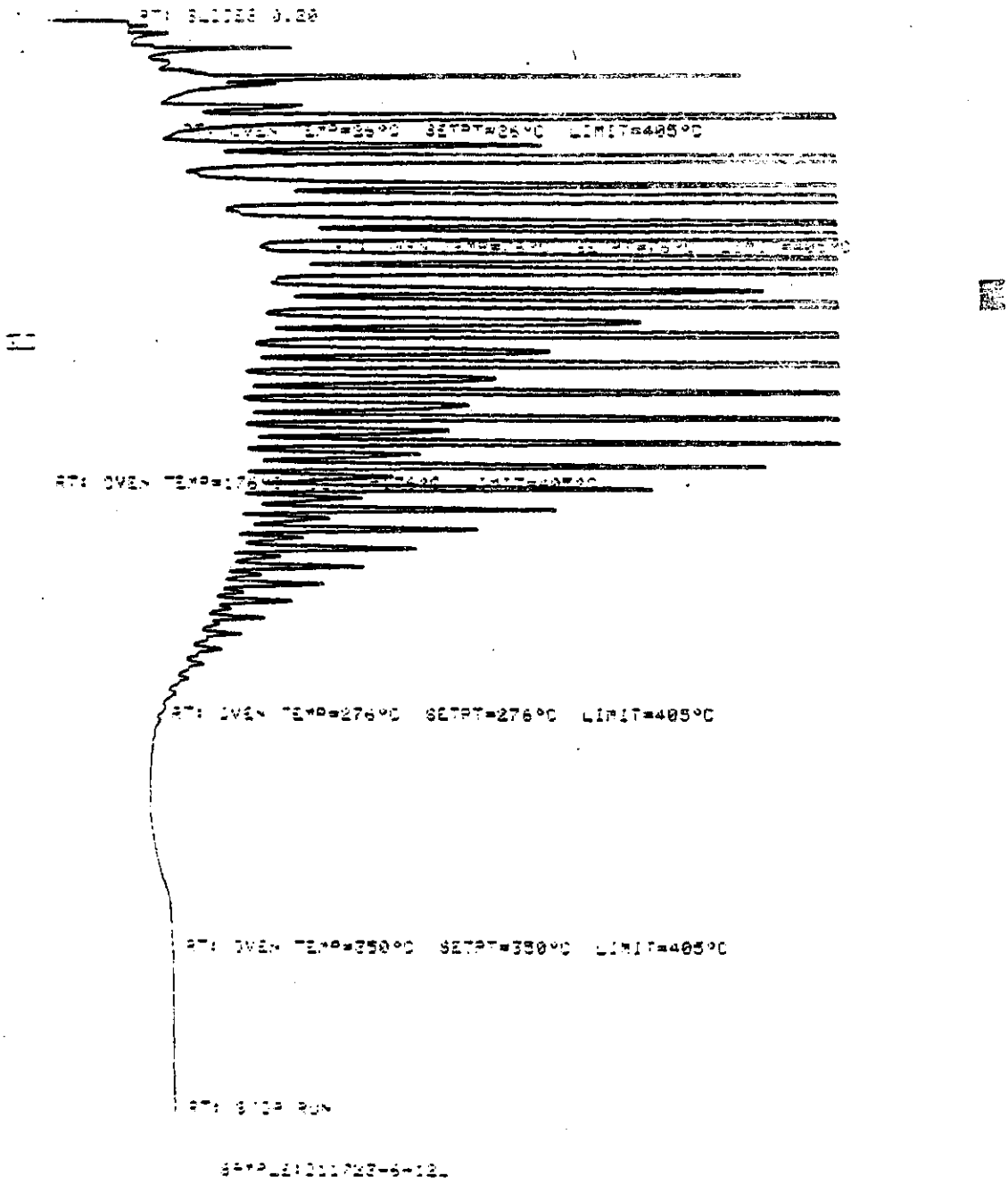
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Fig. 104

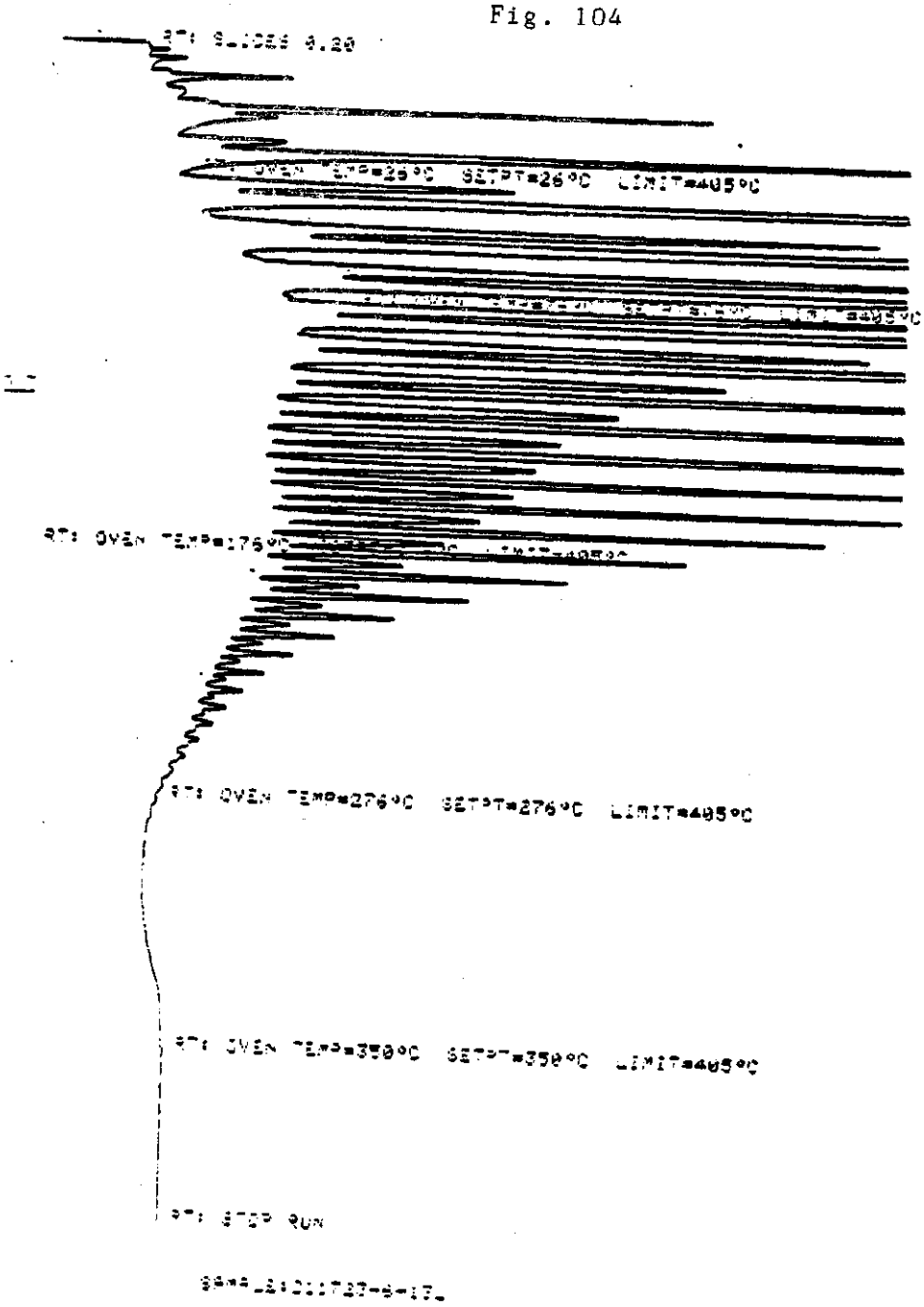
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Fig. 105

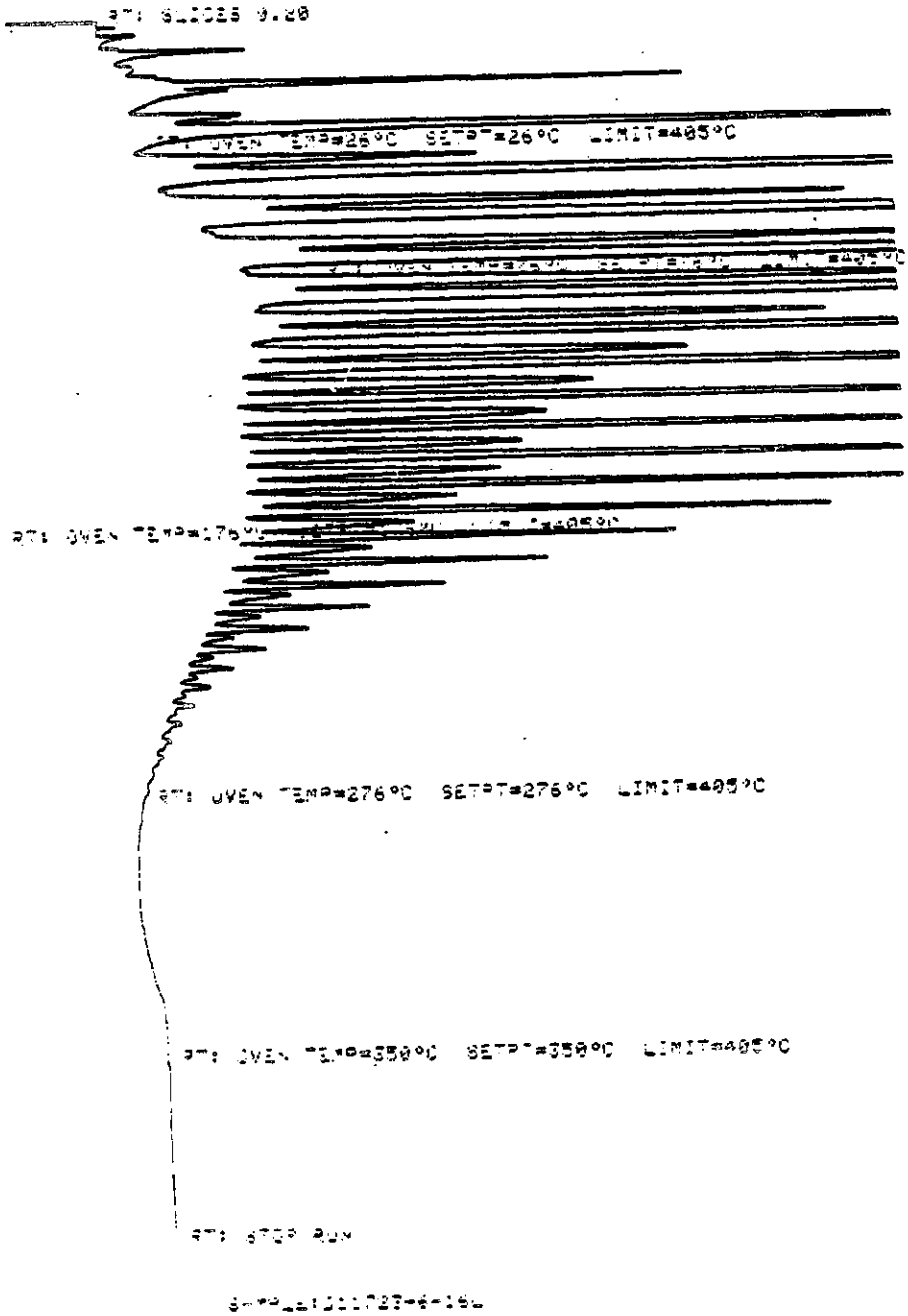


TABLE 19 RESULT OF SYNGAS OPERATION

RUN NO. 11723-06
CATALYST CO/TH+UCC-103+UCC-108 #11684-50 250 CC 111.6 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 300 GHSV

	11723-06-01	723-06-02	723-06-03	723-06-04	723-06-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.5	26.5	42.0	48.8	67.5
PRESSURE,PSIG	300	294	299	292	298
TEMP. C	275	275	275	275	275
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	18.50	8.17	23.50	6.75	25.50
EFFLNT GAS LITER	634.65	251.00	786.12	237.19	908.88
GM AQUEOUS LAYER	139.50	69.45	199.85	57.95	218.94
GM OIL	41.89	19.16	55.13	14.12	53.33
MATERIAL BALANCE					
GM ATOM CARBON %	92.35	84.47	89.70	92.06	90.06
GM ATOM HYDROGEN %	91.63	90.70	94.92	97.25	95.52
GM ATOM OXYGEN %	93.49	89.21	93.66	96.52	94.38
RATIO CHX/(H2O+CO2)	0.9677	0.8735	0.8953	0.8838	0.8791
RATIO X IN CHX	2.4997	2.4631	2.4864	2.5165	2.4310
USAGE H2/CO PRODT	1.7202	1.7741	1.7781	1.7827	1.9167
RATIO CO2/(H2O+CO2)	0.1901	0.1492	0.1541	0.1556	0.0918
K SHIFT IN EFFLNT	0.09	0.07	0.08	0.08	0.05
CONVERSION					
ON CO %	44.33	45.38	44.30	43.32	38.50
ON H2 %	77.92	79.63	78.15	77.21	73.89
ON CO+H2 %	61.06	63.11	61.70	60.73	56.72
PRDT SELECTIVITY,WT %					
CH4	20.42	18.78	19.86	21.11	17.23
C2 HC'S	3.90	3.45	3.58	3.88	3.25
C3H8	5.41	5.21	5.25	5.58	4.88
C3H6=	1.81	1.73	1.81	1.81	1.80
C4H10	4.56	4.33	4.36	4.68	4.22
C4H8=	4.10	3.78	3.75	3.82	3.66
C5H12	4.69	4.56	4.74	4.76	4.74
C5H10=	4.14	4.00	3.99	3.99	3.88
C6H14	4.69	4.67	4.89	4.96	5.17
C6H12= & CYCLO'S	3.36	3.11	3.10	3.06	3.15
C7+ IN GAS	13.63	14.58	14.03	15.09	18.40
LIQ HC'S	29.28	31.78	30.65	27.26	29.62
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	40.20	37.30	38.61	40.88	35.04
C5 -420 F	47.65	49.44	48.60	47.44	52.28
420-700 F	11.27	11.91	11.49	10.26	11.15
700-END PT	0.88	1.36	1.31	1.42	1.54
C5+-END PT	59.80	62.70	61.39	59.12	64.96
ISO/NORMAL MOLE RATIO					
C4	0.0492	0.0451	0.0416	0.0428	0.0384
C5	0.0917	0.0831	0.0803	0.0848	0.0806
C6	0.1861	0.1777	0.1720	0.1753	0.1416
C4=	0.1325	0.1368	0.1404	0.1431	0.1314
PARAFFIN/OLEFIN RATIO					
C3	2.8440	2.8666	2.7767	2.9370	2.5807
C4	1.0746	1.1039	1.1226	1.1841	1.1140
C5	1.1029	1.1089	1.1551	1.1605	1.1879
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7707		0.7798		0.7839
RATIO CH4/(1-A)**2	3.8823		4.0948		3.6878
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY		CLDY		CLDY
DENSITY	0.731		0.727		0.738
N, REFRACTIVE INDEX	1.4221		1.4206		1.4209
SIMULT'D DISTILATN					
10 WT % @ DEG F	255		255		256
16	265		265		283
50	385		385		393
84	571		578		589
90	617		629		641
RANGE(16-84 %)	306		313		306
WT % @ 420 F	58.50	58.25	58.25	57.17	57.17
WT % @ 700 F	97.00	95.73	95.73	94.80	94.80

TABLE 20 RESULT OF SYNGAS OPERATION

RUN NO. 11723-06
CATALYST CO/TH+UCC-103+UCC-108 #11684-50 250 CC 111.6 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 300 GHSV

	11723-06-06	723-06-08	723-06-09	723-06-10	723-06-11
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	74.5	113.0	120.0	137.0	143.5
PRESSURE,PSIG	301	298	302	294	294
TEMP. C	269	268	268	269	267
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	7.00	24.00	7.00	24.00	6.50
EFFLNT GAS LITER	277.73	956.65	272.20	966.70	272.05
GM AQUEOUS LAYER	52.34	175.49	56.58	194.00	53.12
GM OIL	11.58	40.10	11.67	40.01	11.64
MATERIAL BALANCE					
GM ATOM CARBON %	96.01	95.35	94.21	95.15	96.90
GM ATOM HYDROGEN %	95.02	95.75	98.44	99.21	102.19
GM ATOM OXYGEN %	97.97	95.90	97.40	98.71	100.48
RATIO CHX/(H2O+CO2)	0.9402	0.9825	0.9083	0.8955	0.8957
RATIO X IN CHX	2.5126	2.4974	2.5267	2.5088	2.5046
USAGE H2/CO PRODT	1.8805	1.9273	1.9030	1.9425	1.9648
RATIO CO2/(H2O+CO2)	0.1239	0.1081	0.1143	0.0959	0.0875
K SHIFT IN EFFLNT	0.06	0.06	0.06	0.05	0.05
CONVERSION					
ON CO %	36.28	36.03	37.74	35.58	34.77
ON H2 %	70.87	69.71	71.83	69.78	68.21
ON CO+H2 %	53.48	52.91	55.16	53.04	51.93
PRDT SELECTIVITY,WT %					
CH4	20.57	20.61	21.78	21.02	20.76
C2 HC'S	3.97	3.92	3.97	3.91	4.07
C3H8	5.79	4.94	5.33	5.06	5.12
C3H6=	2.11	2.40	1.99	2.00	2.10
C4H10	4.98	4.15	4.39	4.22	4.21
C4H8=	4.29	4.36	4.08	3.93	3.95
C5H12	5.22	4.36	4.61	4.47	4.50
C5H10=	4.34	4.28	4.12	4.10	4.05
C6H14	5.16	4.69	4.96	5.05	4.75
C6H12= & CYCLO'S	3.08	3.28	3.15	3.20	3.05
C7+ IN GAS	16.74	19.12	18.31	18.93	17.62
LIQ HC'S	23.75	23.89	23.31	24.11	25.81
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	41.71	40.38	41.55	40.13	40.22
C5 -420 F	47.63	48.47	47.74	48.80	49.07
420-700 F	9.24	9.55	9.03	9.34	8.95
700-END PT	1.43	1.60	1.67	1.73	1.76
C5+-END PT	58.29	59.62	58.45	59.87	59.78
ISO/NORMAL MOLE RATIO					
C4	0.0368	0.0537	0.0383	0.0372	0.0375
C5	0.0738	0.0893	0.0758	0.0743	0.0767
C6	0.1233	0.1467	0.1368	0.1304	0.1254
C4=	0.1326	0.1219	0.1367	0.1316	0.1318
PARAFFIN/OLEFIN RATIO					
C3	2.6223	1.9629	2.5554	2.4202	2.3330
C4	1.1213	0.9189	1.0386	1.0351	1.0282
C5	1.1704	0.9891	1.0878	1.0596	1.0799
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.7831		0.7848	
RATIO CH4/(1-A)**2		4.3791		4.5396	
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLDY		CLDY	
DENSITY		0.752		0.728	
N, REFRACTIVE INDEX		1.4230		1.4223	
SIMULT'D DISTILATN					
10 WT % @ DEG F		261		261	
16		301		301	
50		414		413	
84		612		615	
90		664		669	
RANGE(16-84 %)		311		314	
WT % @ 420 F	55.11	53.33	54.09	54.09	58.50
WT % @ 700 F	94.00	93.31	92.82	92.82	93.19

TABLE 21 RESULT OF SYNGAS OPERATION

RUN NO. 11723-06
CATALYST CO/TH+UCC-103+UCC-108 #11684-50 250 CC 111.6 GM
FEED H2:CO:ARGON OF 50:50: 0 @ 1260 CC/MN OR 300 GHSV

	11723-06-12	723-06-13	723-06-14	723-06-15	723-06-16
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	161.0	168.5	186.6	189.5	211.0
PRESSURE,PSIG	297	290	299	300	293
TEMP. C	277	274	273	273	274
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	24.00	7.50	25.00	3.50	25.00
EFFLNT GAS LITER	931.95	283.25	968.25	127.85	961.80
GM AQUEOUS LAYER	196.12	59.92	199.74	28.23	201.68
GM OIL	42.99	11.66	38.88	5.72	40.83
MATERIAL BALANCE					
GM ATOM CARBON %	98.91	94.34	93.53	90.60	95.02
GM ATOM HYDROGEN %	102.72	98.19	97.26	95.08	98.21
GM ATOM OXYGEN %	100.20	96.12	97.52	94.36	97.85
RATIO CHX/(H2O+CO2)	0.9652	0.9492	0.8857	0.8924	0.9199
RATIO X IN CHX	2.5892	2.5543	2.5881	2.5563	2.5631
USAGE H2/CO PRODT	1.8114	1.8799	1.8852	1.8866	1.8837
RATIO CO2/(H2O+CO2)	0.1671	0.1320	0.1278	0.1232	0.1285
K SHIFT IN EFFLNT	0.09	0.07	0.07	0.06	0.07
CONVERSION					
ON CO %	42.76	40.15	37.84	39.15	38.89
ON H2 %	75.73	74.23	72.47	74.11	73.60
ON CO+H2 %	59.56	57.53	55.49	57.05	56.53
PRDT SELECTIVITY,WT %					
CH4	24.50	22.85	24.53	23.04	23.31
C2 HC'S	4.55	4.15	4.40	4.18	4.22
C3H8	5.83	5.80	5.55	5.62	5.68
C3H6=	2.11	2.26	1.87	1.86	1.88
C4H10	4.75	4.87	4.68	4.58	4.63
C4H8=	3.73	4.00	3.88	3.45	3.49
C5H12	4.79	4.74	5.03	4.69	4.74
C5H10=	3.77	3.77	3.95	3.67	3.72
C6H14	5.04	4.98	5.24	5.13	5.19
C6H12= & CYCLO'S	2.74	2.76	2.96	2.90	2.93
C7+ IN GAS	16.37	19.20	15.80	17.80	18.01
LIQ HC'S	21.84	20.61	22.11	23.09	22.19
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	45.45	43.94	44.91	42.72	43.22
C5 -420 F	45.48	47.47	45.96	47.83	47.70
420-700 F	7.58	7.35	7.90	8.26	7.94
700-END PT	1.49	1.24	1.23	1.18	1.14
C5+-END PT	54.55	56.06	55.09	57.28	56.78
ISO/NORMAL MOLE RATIO					
C4	0.0506	0.0621	0.0382	0.0410	0.0410
C5	0.0887	0.0856	0.0821	0.0815	0.0815
C6	0.1757	0.1546	0.1420	0.1442	0.1442
C4=	0.1545	0.1500	0.1442	0.1629	0.1629
PARAFFIN/OLEFIN RATIO					
C3	2.6420	2.4468	2.8365	2.8854	2.8854
C4	1.2295	1.1737	1.1657	1.2794	1.2794
C5	1.2346	1.2218	1.2371	1.2406	1.2406
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7814		0.7787		0.7707
RATIO CH4/(1-A)**2	5.1258		5.0073		4.4349
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY		CLDY		CLDY
DENSITY	0.720		0.739		0.733
N, REFRACTIVE INDEX	1.4204		1.4204		1.4201
SIMULT'D DISTILATN					
10 WT % @ DEG F	255		257		257
16	267		288		287
50	387		391		387
84	599		591		578
90	658		649		636
RANGE(16-84 %)	332		303		291
WT % @ 420 F	58.50	58.33	58.72	59.10	59.10
WT % @ 700 F	93.19	94.00	94.44	94.88	94.88

VI. Run 5 (11723-04) with Catalyst 5 (Co/Th/X_6 + UCC-103)

This catalyst is similar to Eleventh Quarter Catalyst 7 (Run 10225-16) except that the metal component contains the additive X_6; it is intended to isolate the effect of X_6 in this type of catalyst formulation. Comparison of the results from Tenth Quarter Catalyst 3 (Run 10112-15), which contained no additive, to the results from Eleventh Quarter Catalyst 4 (Run 11677-03), formulated in the same way but with the addition of X_6, showed that X_6 substantially improved the latter catalyst's selectivity.

The thorium-promoted cobalt oxide was formed in close contact with UCC-103, then further promoted with X_6. The mixture was bonded with 15 weight percent silica and formed as an extrudate. The final catalyst contained 8.5 percent cobalt and 0.2 percent X_6.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 106-109 for this catalyst and in Figs. 110-113 for Run 11677-03. Simulated distillations of the C_5^+ product are plotted in Figs. 114-117. Carbon number product distributions are plotted in Figs. 118-127. Chromatograms from simulated distillations are reproduced in Figs. 128-137. Detailed material balances appear in Tables 22-25 for this catalyst and in Tables 26-27 for Run 11677-3.

This catalyst, unlike Catalysts 1-4 and the Eleventh Quarter Catalyst 7, deactivated significantly at the beginning of the run. During the first 2.5 days on stream, syngas conversion dropped from the initial 72 percent to 63 percent; in the same period, some of the limited water gas shift activity was lost as well, from 35 percent of oxygen rejected as CO_2 to 25 percent, and the H_2:CO usage ratio rose from 1.4:1 to 1.6:1. During the next two days, when the temperature was maintained at 270C, both conversion and water gas shift activity held steady. All of these findings are fairly typical of Co/Th catalysts without the additive X_6. Eleventh Quarter Catalyst 4 (Run 11677-03), with a metal component similar to this one and a similar Molecular Sieve, UCC-101, but without the intimate contact between metal component and shape selective component, was less active than this catalyst even though it contained 50 percent more cobalt. Its conversion, initially 59 percent, dropped to 53 percent after 120 hours on stream and remained at that level for the next 4 days. Its water gas shift activity was also much lower than that of the present catalyst, and lower than typical values for catalysts of similar formulation, with only about 6 percent of the oxygen rejected as CO_2 and a correspondingly high H_2:CO usage ratio of 2.0:1. The catalyst in Run 10225-16, with 17 percent more cobalt, had only 13 percent higher activity than the present catalyst but it did have comparable water gas shift activity with initially 40 percent and finally 24 percent of the oxygen

rejected as CO_2. The present catalyst, in other words, is free of the loss of water gas shift activity which in previous tests has been a major undesirable effect of the X_6 additive.

When the test temperature was lowered from 270C to 260C, conversion dropped to 52 percent; but during the last four days of the test, instead of deactivating with time, as usually happens, conversion actually increased to 55 percent by the end of the run. As usual when the temperature was lowered, the water gas shift activity dropped in relation to the Fischer-Tropsch activity, so that at 260C only 12 percent of the oxygen was rejected as CO_2 and the H_2:CO usage ratio was up to almost 1.9:1.

The catalyst's selectivity followed a pattern similar to that of its conversion. Methane production, initially high at 17 percent, rose to 24.5 percent at 115 hours on stream (which is actually higher than was produced in Run 10225-16), dropped to 21 percent when the temperature was lowered to 260C, then fell slowly to 20 percent at the end of the run. In contrast, the previous catalyst tested with X_6 (Eleventh Quarter Catalyst 4, Run 11677-03) produced 14 percent methane initially and 18 percent after 214 hours on stream--not the lowest or most stable methane production obtained so far, but remarkably low and stable for that catalyst's method of preparation. The present catalyst's methane production was more like that of Tenth Quarter Catalyst 3 (Run 10112-15), which was an acceptable 15 percent initially but up to 24 percent at the end of the run.

Production of C_2-C_4 hydrocarbons was also high for a cobalt

catalyst--more like that of an iron catalyst and substantially higher than that of either of the Eleventh Quarter Catalysts 4 or 7.

Because of the high methane and C_2-C_4 yield, production of C_5^+ hydrocarbons was relatively low, again more like that of an iron rather than a cobalt catalyst. C_5^+ production, initially a little over 55 percent, dropped to 47 percent, including 46 percent motor fuels, after 120 hours on stream. At 260C the C_5^+ yield was steady at 50.5 percent, including 50 percent motor fuels.

Almost none of the pentane product was isomerized. The C_4 hydrocarbons were highly paraffinic. Except for the excess methane the Schulz-Flory plots show a straight line, and the chromatograms from the simulated distillations show little if any isomerization of the liquid product. Unlike the previous results in this Quarter, these findings are reflected in the quality of the liquid product, which did contain wax.

Additive X_6, which so dramatically enhanced the effectiveness of Eleventh Quarter Catalyst 4, apparently contributed little or nothing to this catalyst. One possible explanation is that the additive may have been too closely associated with the UCC-103 and not closely enough with the cobalt.

Fig. 106

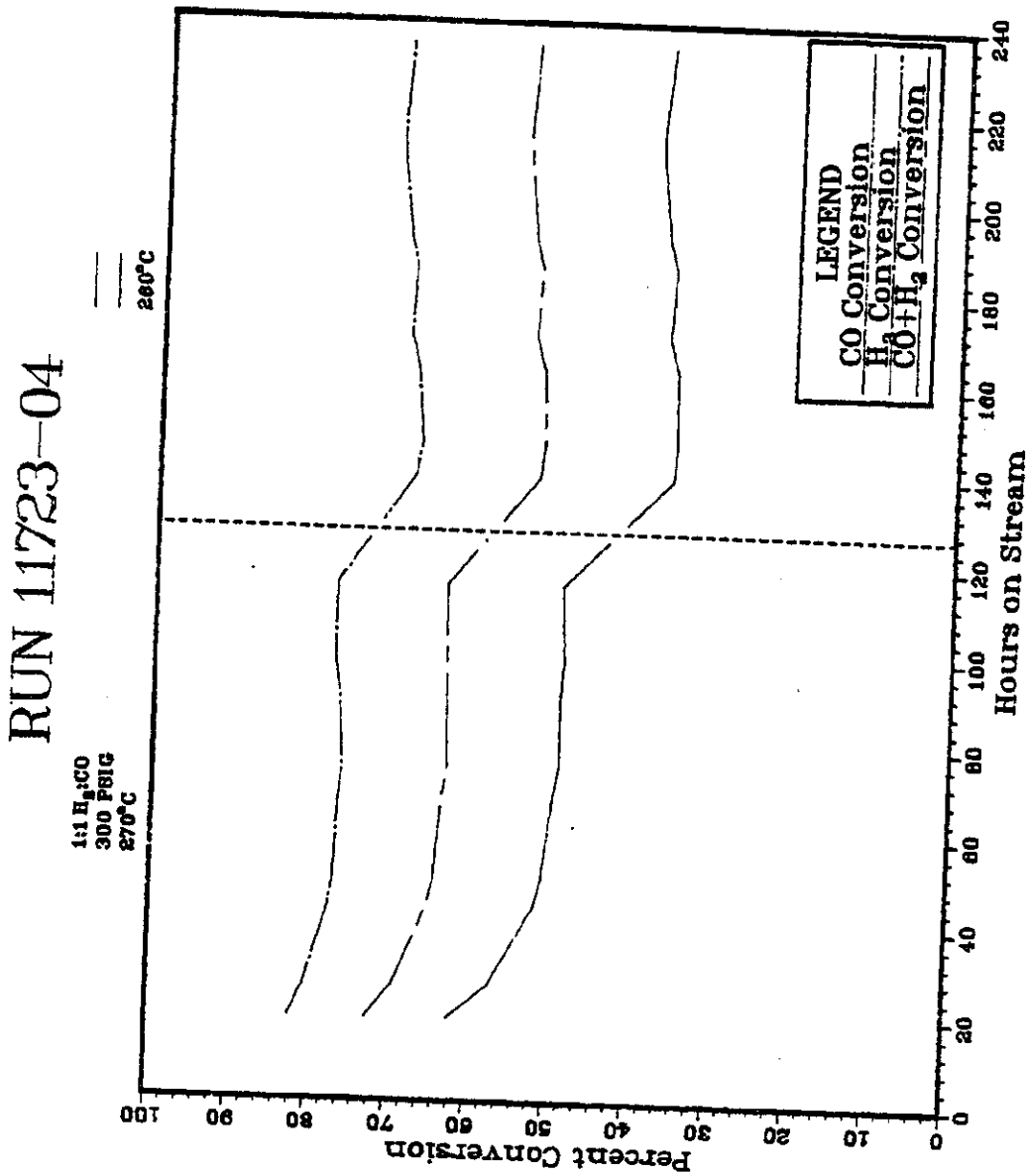

RUN 11723-04
1:1 H2:CO
300 PSIG
270°C
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 107

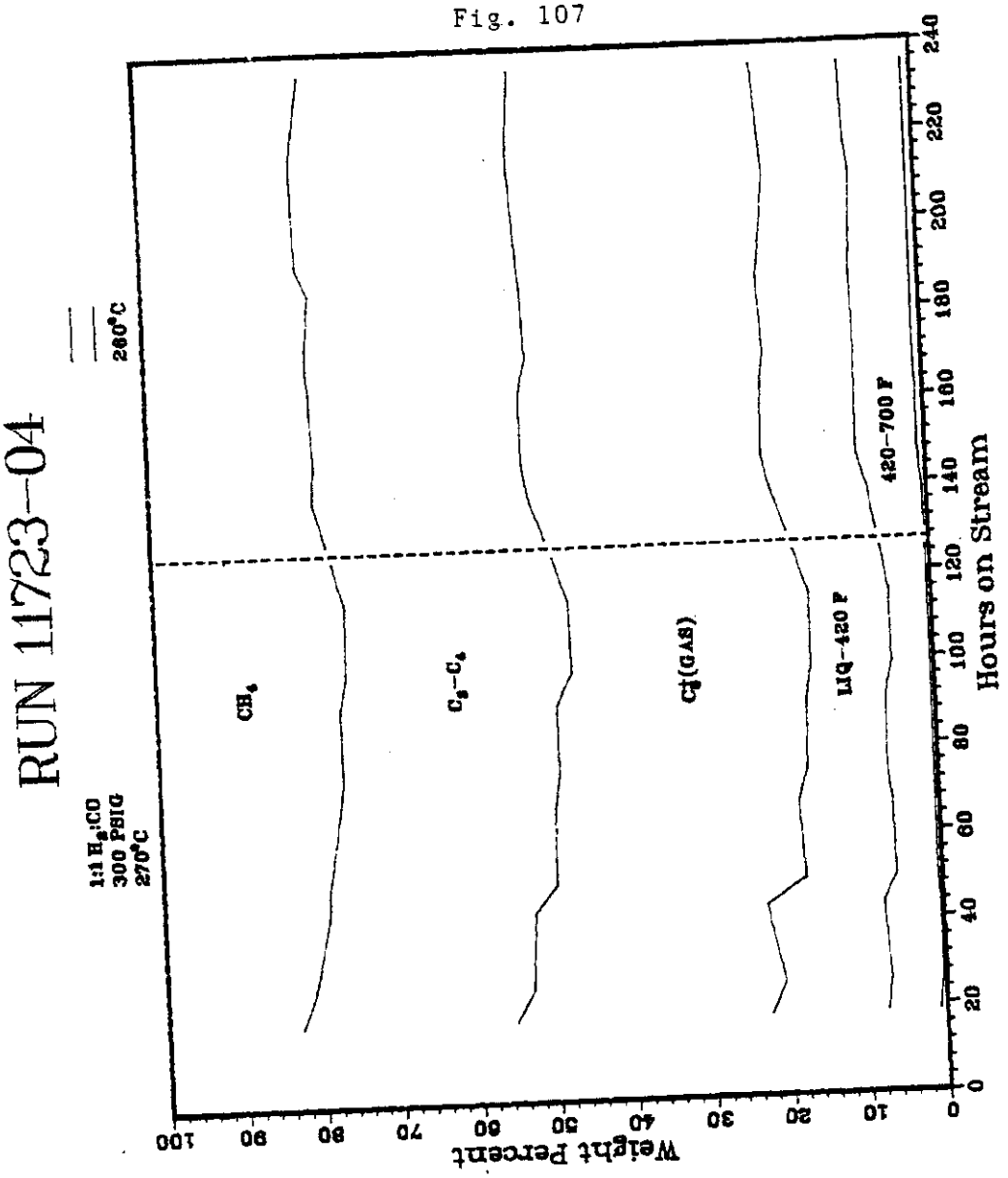

RUN 11723-04
1:1 H2:CO
300 PSIG
270°C
280°C
CH4
C2-C4
C5(GAS)
LIQ-420 F
420-700 F
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 108

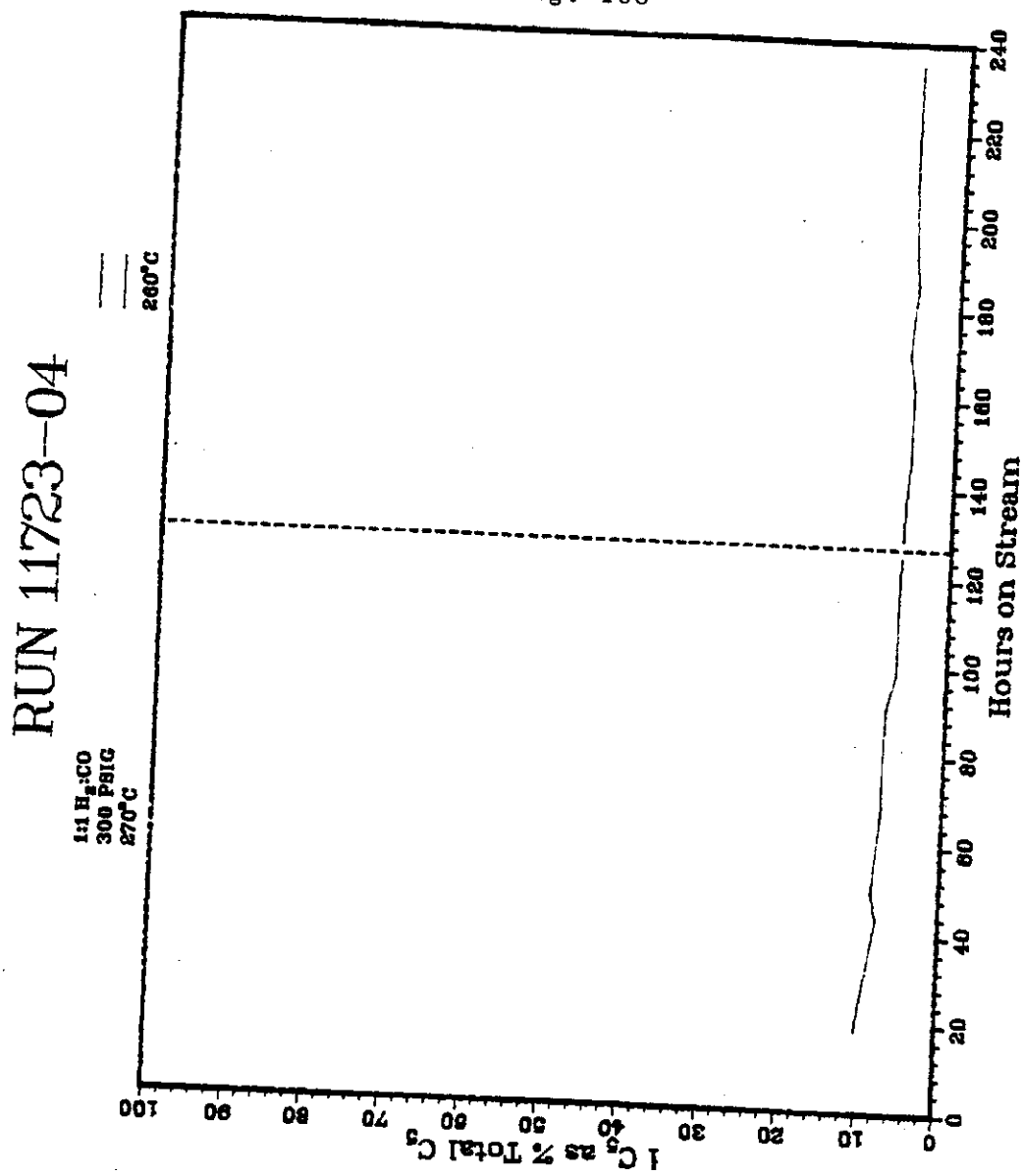
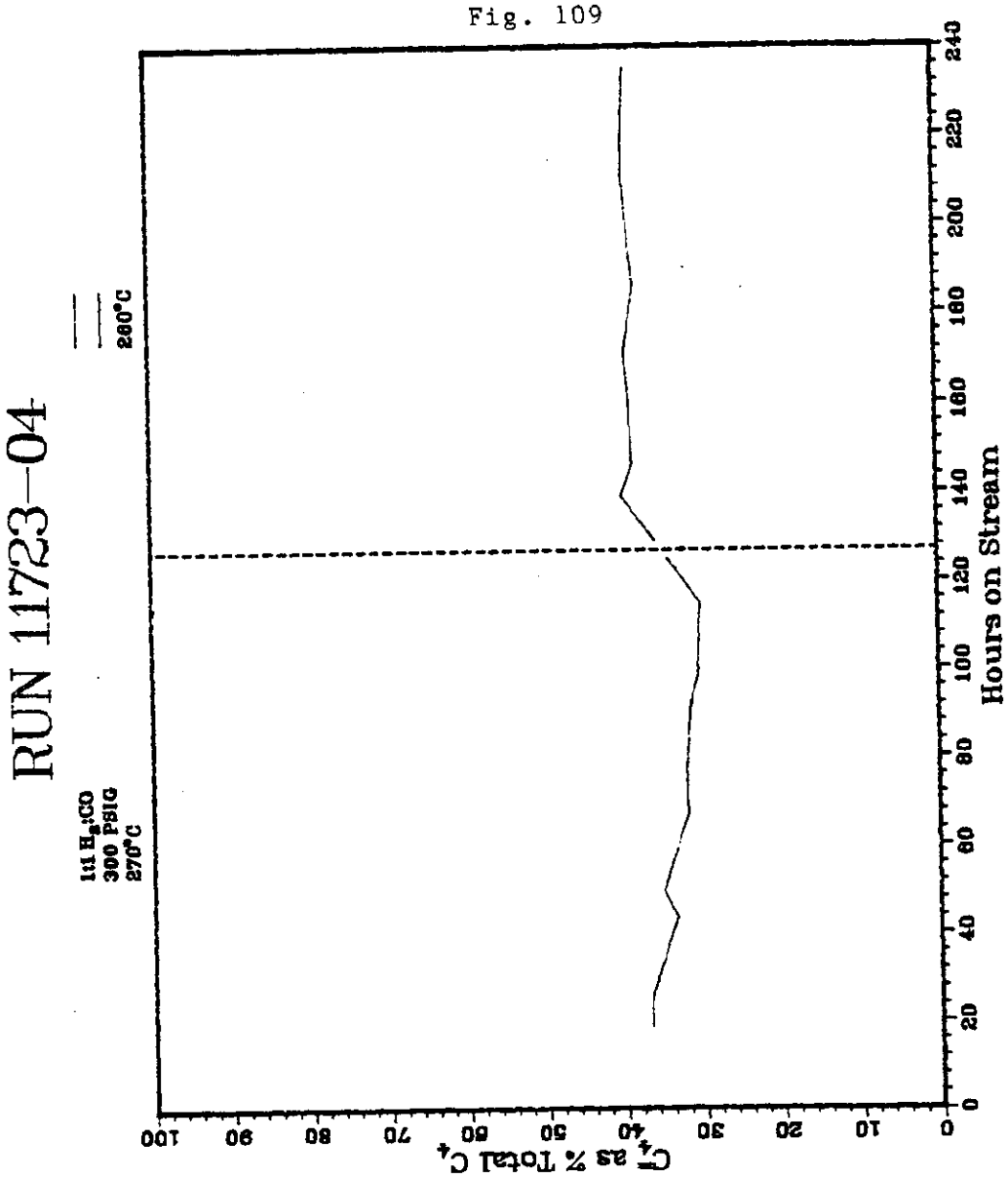

RUN 11723-04
1:1 H2:CO
300 PSIG
270°C
260°C
i C5 as % Total C3
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240

Fig. 109


RUN 11723-04
111 H2:CO
300 PSIG
270°C
280°C
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180
200
220
240