

Fig. 84

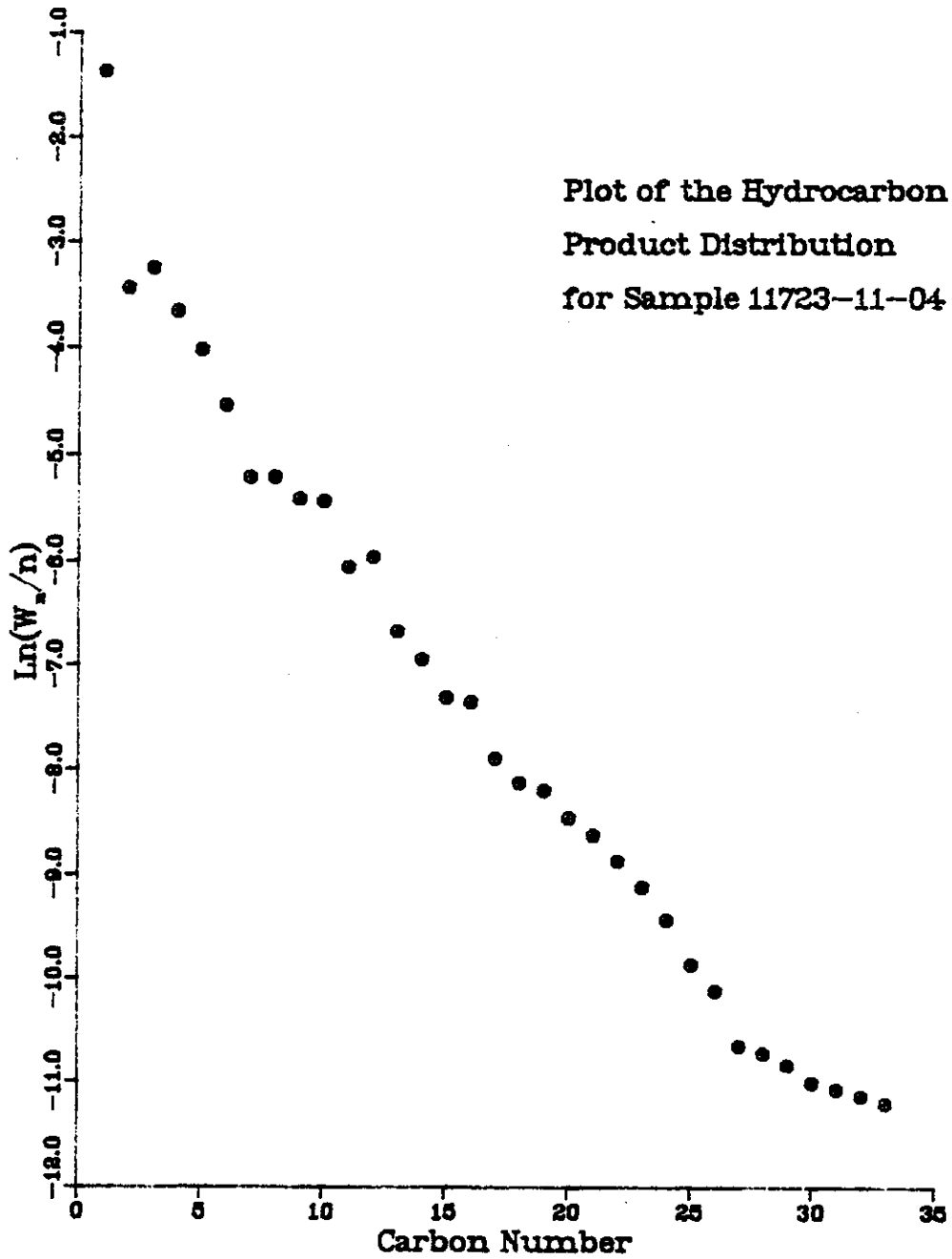
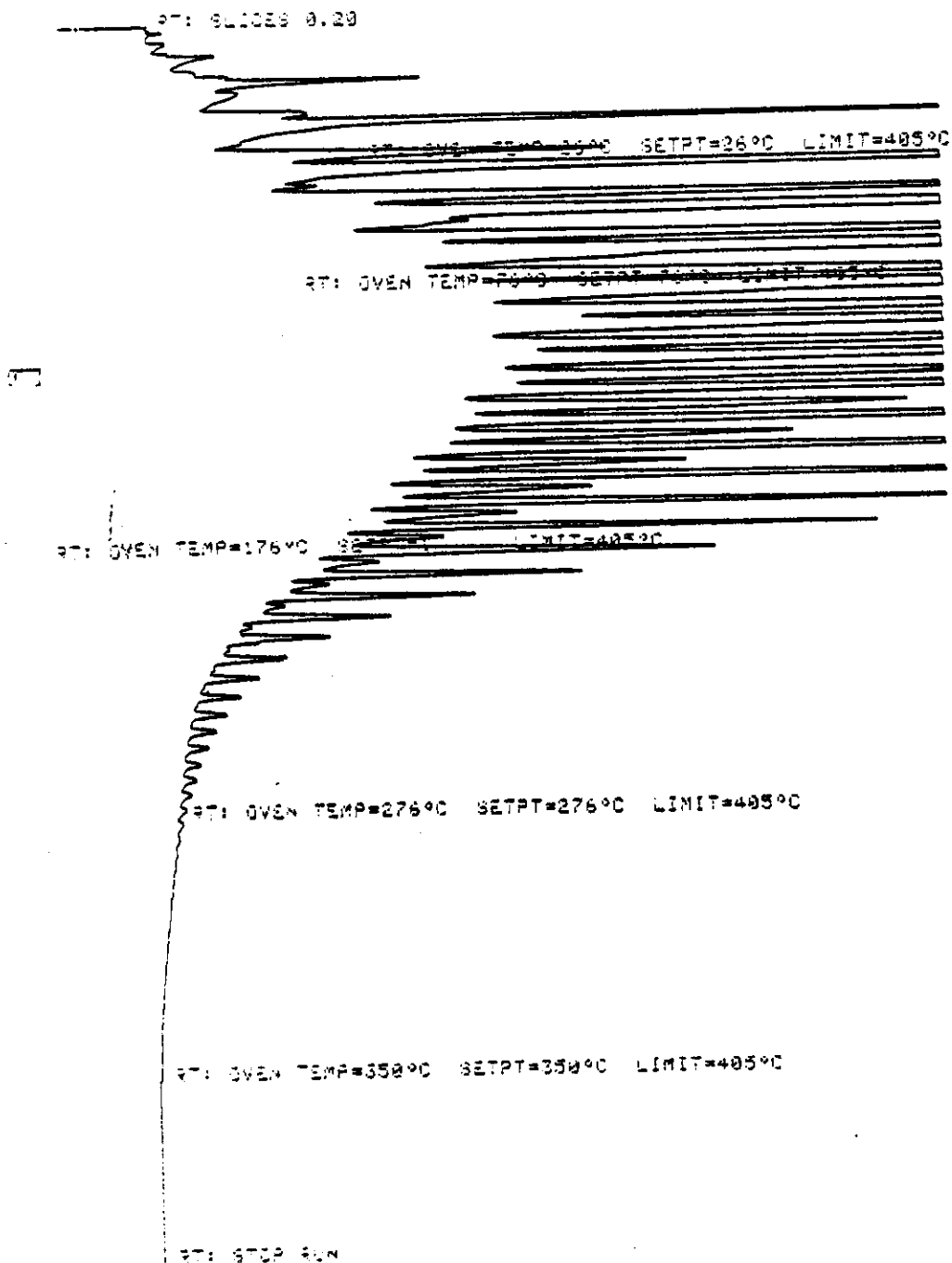
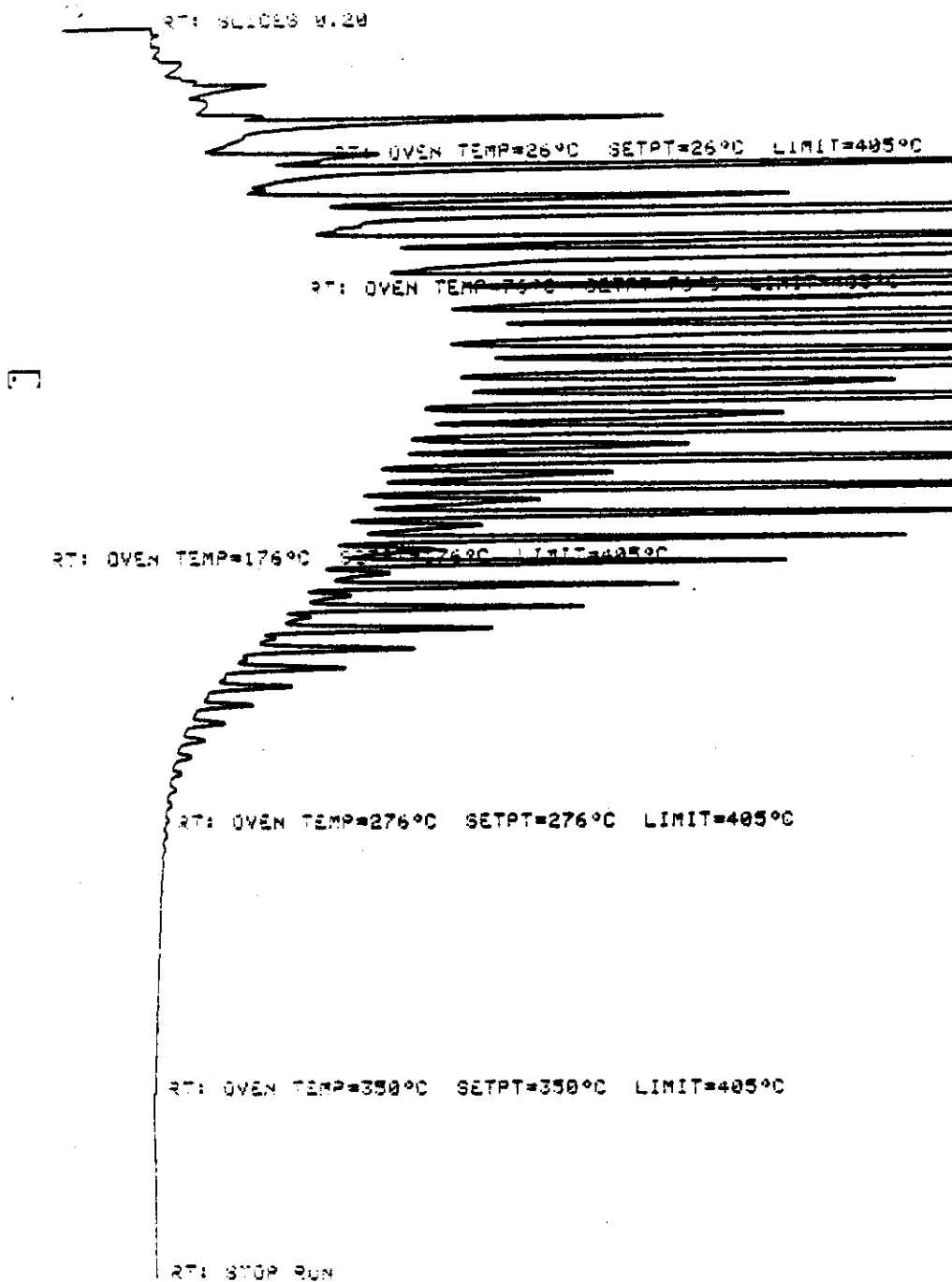


Fig. 85



D 11723-11-2L

Fig. 86



D11723-11-4

Table 14

RESULT OF SYNGAS OPERATION

RUN NO. 11723-11
 CATALYST CoThCu+UCCl01+CuZnAl 250 CC 112.GM (Cat#11684-78C +3.1G)
 FEED H2:CO:ARGON OF 50/50/0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11723-11-01	723-11-02	723-11-03	723-11-04
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	4.17	24.0	32.0	50.0
PRESSURE,PSIG	297	295	295	294
TEMP. C	265	265	264	264
FEED CC/MIN	1260	1260	1260	1260
HOURS FEEDING	4.17	19.83	7.50	25.50
EFFLNT GAS LITER	130.60	976.00	349.25	1209.55
GM AQUEOUS LAYER	28.86	169.71	47.49	161.46
GM OIL	5.75	33.81	7.52	25.57
MATERIAL BALANCE				
GM ATOM CARBON %	79.90	106.30	94.70	95.14
GM ATOM HYDROGEN %	86.52	116.65	100.27	101.43
GM ATOM OXYGEN %	86.15	112.95	98.65	98.62
RATIO CHX/(H2O+CO2)	0.8294	0.8291	0.8656	0.8788
RATIO X IN CHX	2.5004	2.5634	2.6473	2.6303
USAGE H2/CO PRODT	1.5790	1.9490	1.9590	2.0075
FEED H2/CO FRM EFFLNT	1.0829	1.0973	1.0588	1.0661
RESIDUAL H2/CO RATIO	0.5677	0.6205	0.6428	0.6538
RATIO CO2/(H2O+CO2)	0.2820	0.1515	0.1521	0.1302
K SHIFT IN EFFLNT	0.2230	0.1108	0.1153	0.0979
SPECIFIC ACTIVITY SA	1.6435	0.8552	0.7345	0.6828
CONVERSION				
ON CO %	50.94	35.89	31.60	30.46
ON H2 %	74.28	63.75	58.48	57.35
ON CO+H2 %	63.08	50.47	45.42	44.34
PRDT SELECTIVITY,WT %				
CH4	17.35	22.28	24.95	25.39
C2 HC'S	4.61	5.82	6.20	6.39
C3H8	7.53	7.13	7.82	7.55
C3H6=	3.00	3.70	4.19	4.08
C4H10	5.51	4.74	5.14	4.96
C4H8=	4.56	5.01	5.64	5.28
C5H12	5.69	4.79	4.76	4.56
C5H10=	4.09	4.50	4.83	4.42
C6H14	5.48	3.95	4.02	3.67
C6H12= & CYCLO'S	2.45	2.87	2.92	2.73
C7+ IN GAS	19.62	11.93	12.28	13.55
LIQ HC'S	20.10	23.28	17.25	17.42
TOTAL	100.00	100.00	100.00	100.00

Table 14 (continued)

SUB-GROUPING				
C1 -C4	42.57	48.68	53.94	53.65
C5 -420 F	48.45	40.92	37.51	37.71
420-700 F	8.05	9.32	7.61	7.68
700-END PT	0.93	1.08	0.95	0.96
C5+-END PT	57.43	51.32	46.06	46.35
ISO/NORMAL MOLE RATIO				
C4	0.1265	0.0786	0.0756	0.0717
C5	0.2669	0.1211	0.1278	0.1254
C6	0.4683	0.2035	0.1924	0.1970
C4=	0.0324	0.0483	0.0508	0.0526
PARAFFIN/OLEFIN RATIO				
C3	2.3932	1.8380	1.7822	1.7635
C4	1.1671	0.9124	0.8802	0.9067
C5	1.3518	1.0356	0.9584	1.0026
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.7272 ?	0.7495		0.7523
RATIO CH4/(1-A)**2		3.5509		4.1359
LIQ HC COLLECTION				
PHYS. APPEARANCE		CLDY YLW		CLDY YLW
DENSITY		0.7545		0.7629
N, REFRACTIVE INDEX		1.4260		1.4281
SIMULT'D DISTILATN				
10 WT % @ DEG F		270		299
16		303		324
50		409		418
84		572		596
90		625		649
RANGE(16-84 %)		269		272
WT % @ 420 F	55.33	55.33	50.40	50.40
WT % @ 700 F	95.38	95.38	94.50	94.50
		55.33		50.40
		95.38		94.50

NEW FORMAT AUG 29,84

VIII. Run 7 (11723-12) with Catalyst 7
(Co/Th/UCC-103+UCC-101+Cu/Zn/Al)

This catalyst was formulated to test whether part of the Fischer-Tropsch component may migrate to the water gas shift component and deactivate it, one of the hypotheses suggested by the results of the previous run. The cobalt/thorium/UCC-103+UCC-101 extrudate was formed in the same way as Catalyst 1. The water gas shift component was formed into a separate extrudate in the same way as for Catalyst 5 except with 40 percent water gas shift component and 20 percent SiO₂ binder, and UCC-101 making up the balance. The separate Fischer-Tropsch and water gas shift extrudates were then combined in a weight ratio of 4:1. The final mixed catalyst contained 6.7 percent cobalt and 8 percent water gas shift component.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 87-90. Simulated distillations of the C₅⁺ product are plotted in Figs. 91-99. Carbon number product distributions are plotted in Figs. 100-112. Chromatograms from simulated distillations are reproduced in Figs. 113-114. Detailed material balances appear in Tables 15-20.

The water gas shift activity was not significantly better than that of Catalyst 1, which was prepared in the same way but

without the added WGS-active extrudate. There was a little activity at 4.5 hours on stream, with 23 percent of the oxygen rejected as CO₂; but at 21 hours on stream, a time when the water gas shift component alone in Run 5 was quite active and when the usage ratio of Catalyst 1 was 1.75:1 and more than 16 percent of its oxygen was rejected as CO₂, the usage ratio of this catalyst was higher than 1.8:1 and less than 15 percent of the oxygen was rejected as CO₂. Paradoxically, the catalyst with the added water gas shift component was actually lower in water gas shift activity than a similar catalyst without it.

As to conversion, during the first part of the run the catalyst deactivated at about one percent every 15 hours, somewhat more rapidly than with Catalyst 1. At about 150 hours on stream, however, its stability improved considerably, and the run was therefore extended to 300 hours. During the last 150 hours the deactivation rate was down to one percent every 74 hours on stream.

The catalyst's selectivity declined steadily throughout the run. Methane production was initially 11 percent, nearly 16 percent at the middle of the run, and more than 18 percent at the end; like the conversion, the loss of selectivity slowed substantially during the last half of the run. Production of C₂-C₄ rose slightly over the length of the run, so that the production of C₅⁺ fell at a faster rate than the methane's rate of increase. The yield of motor fuel, which was reasonably good at first, with diesel and gasoline making up 73 percent of total hydrocarbons,

decreased by the end of the run to 62 percent. In contrast to some of the previous runs, the ratio of diesel to gasoline decreased slightly during the test.

The olefin content of the product was slightly lower than usual for this type of Fischer-Tropsch catalyst. In the 4.5 hour sample the pentane was fairly well isomerized, but for the rest of the run the isomerization fell off to its usual low level.

It may be that intermediates from the Fischer-Tropsch synthesis itself, possibly olefins, are deactivating the water gas shift component in these catalysts. If this is in fact the case, there are two ways in which it might be corrected. One would be to place the water gas shift component in an acidic Molecular Sieve, which might prevent the olefins from deactivating the water gas shift component. The other would be to place it in a Molecular Sieve with apertures of a size which will admit hydrogen, carbon monoxide, carbon dioxide and water, but not the larger hydrocarbons.

Fig. 87

RUN 11723-12

111 H₂CO
300 PSIG
270°C

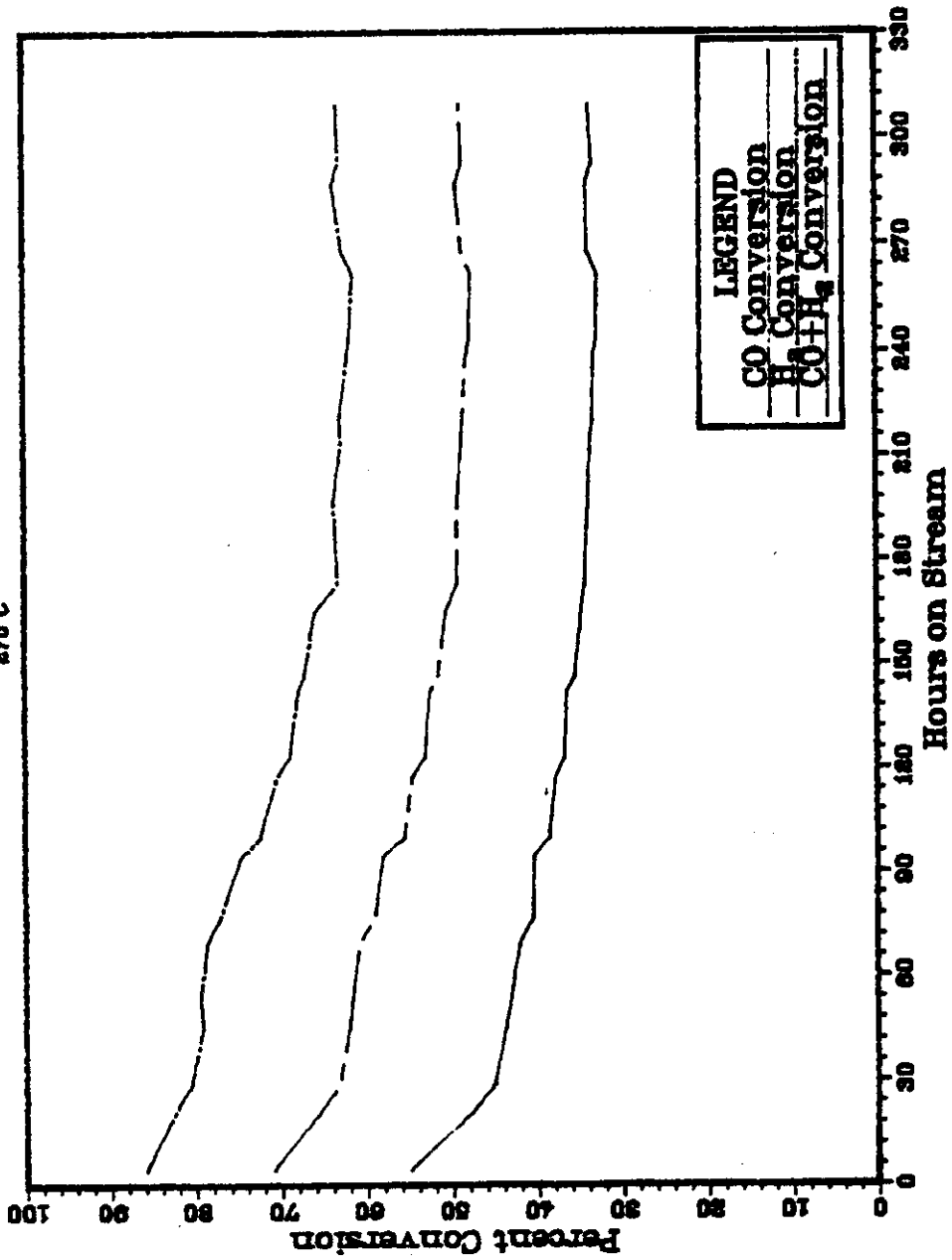


Fig. 88

RUN 11723-12

111 H₂CO
300 PSIG
870°C

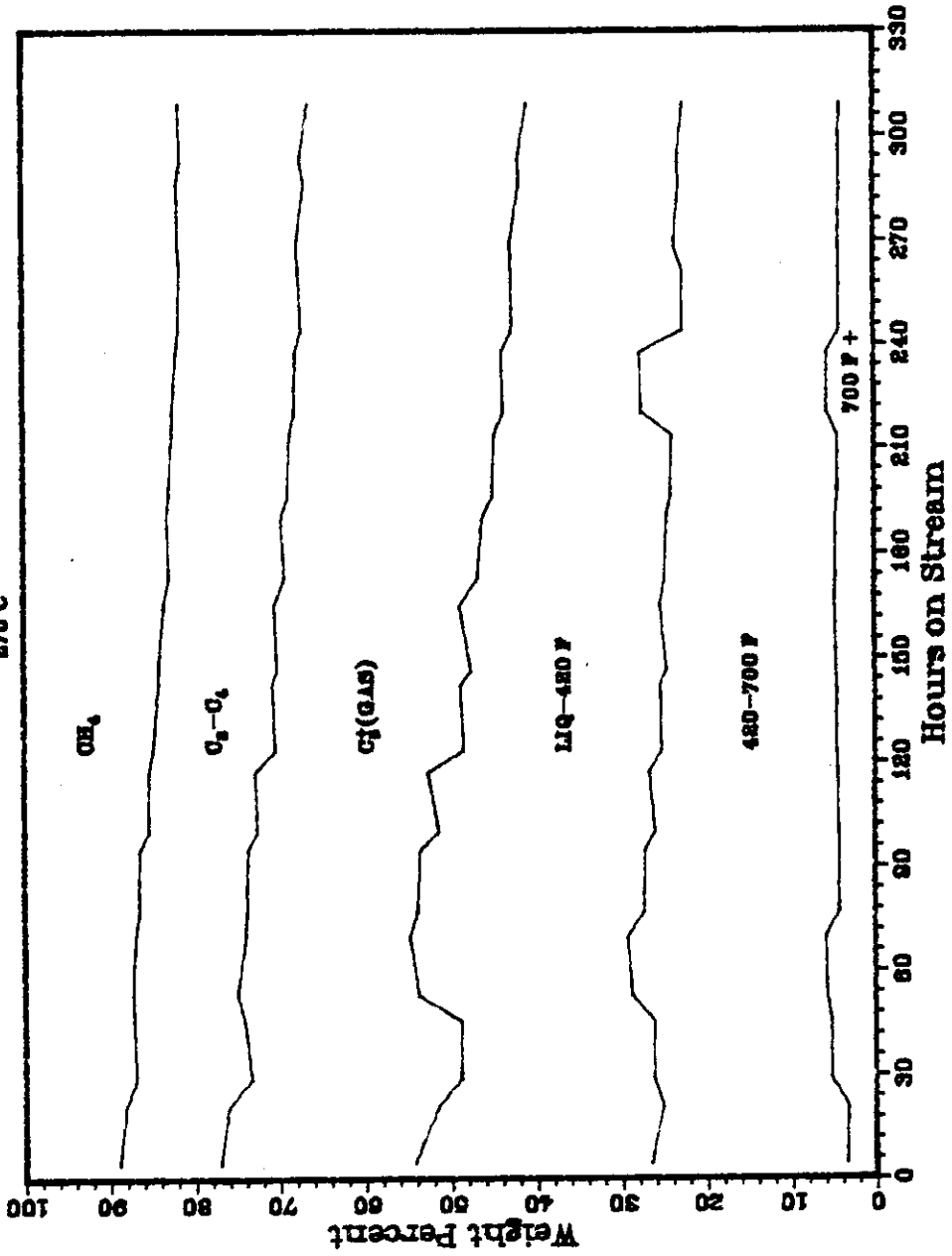


Fig. 89

RUN 11723-12

1:1 H₂O
300 PSIG
270°C

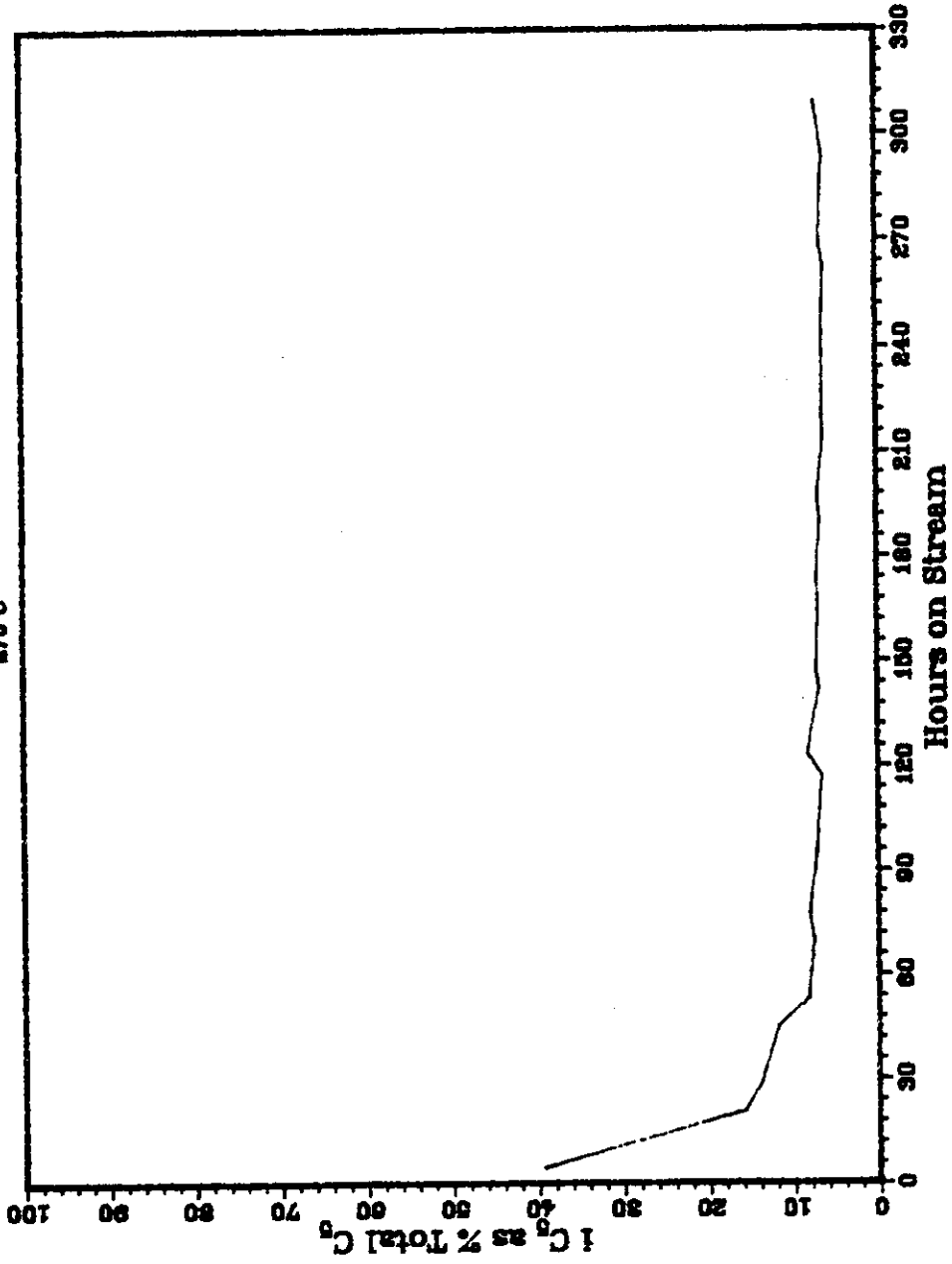


Fig. 90

RUN 11723-12

111 K₂CO₃
300 PMIG
870°C

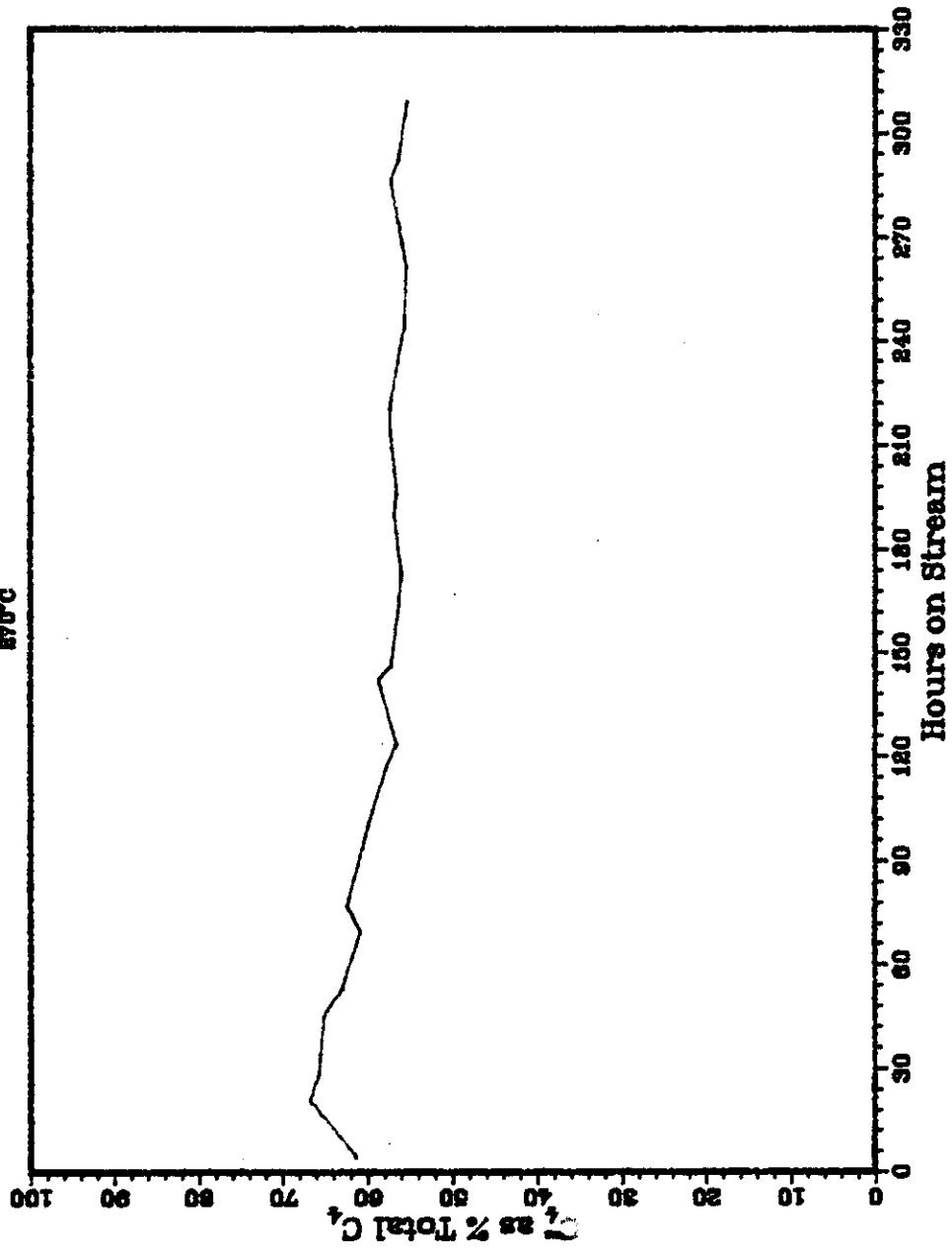


Fig. 91

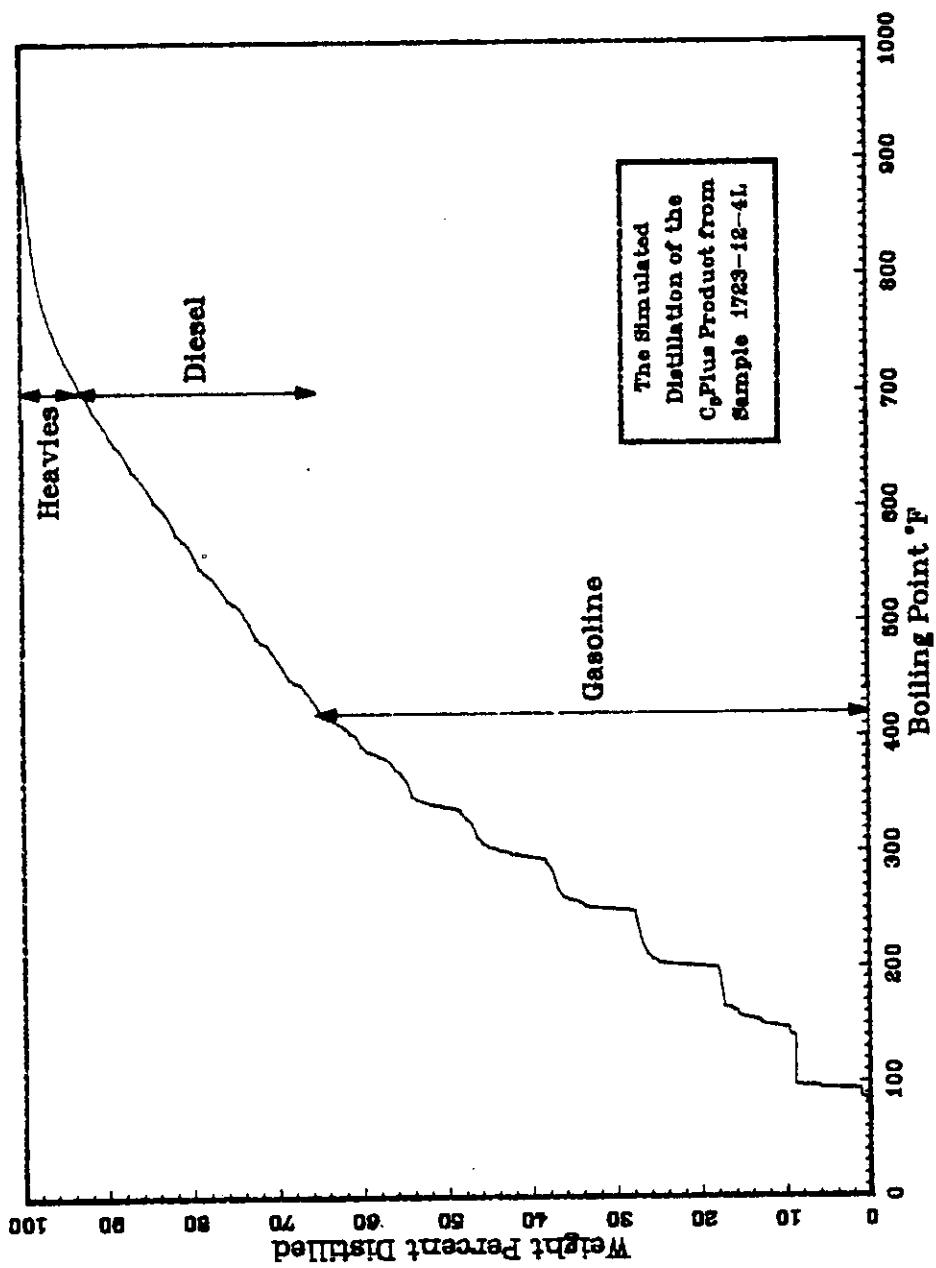


Fig. 92

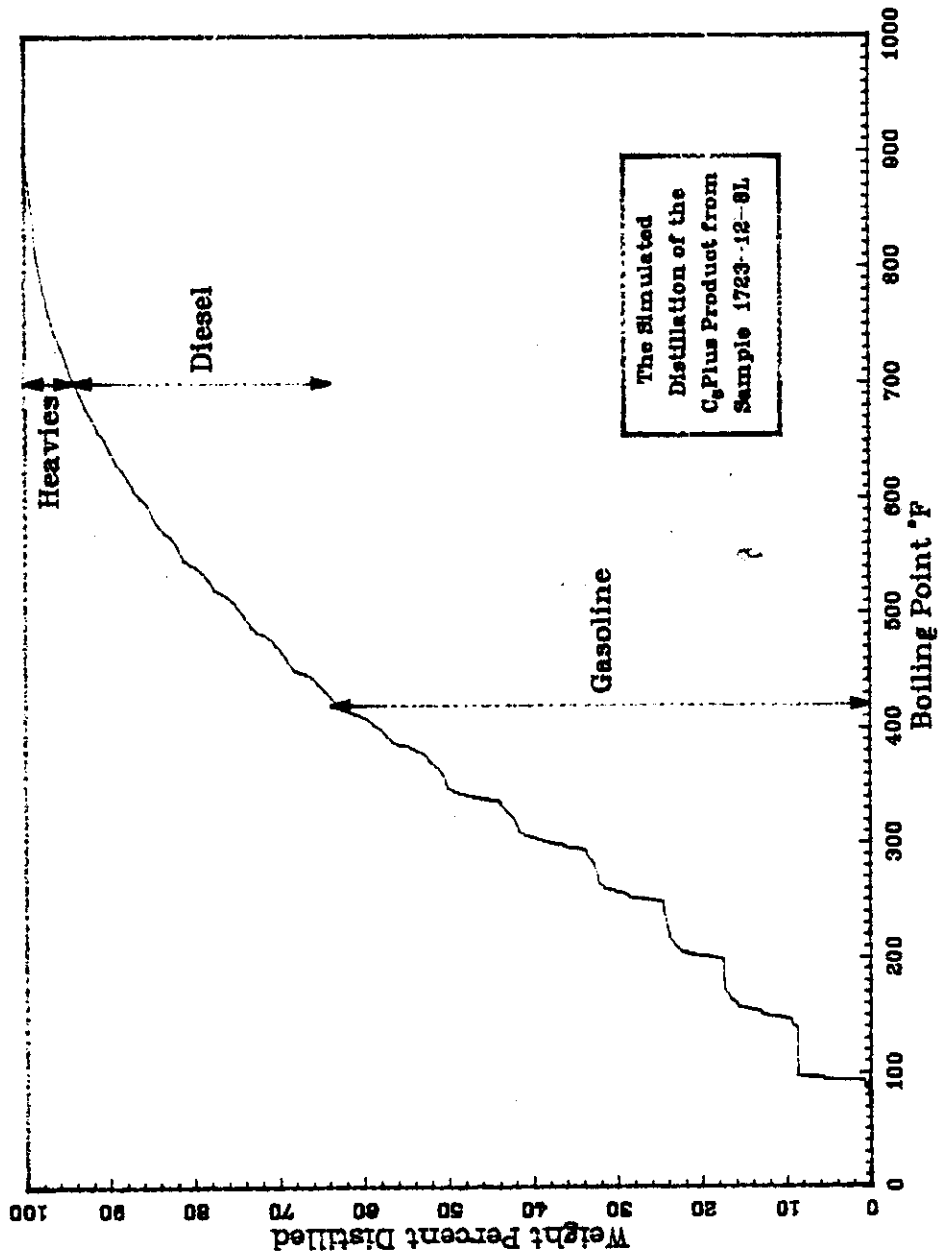


Fig. 93

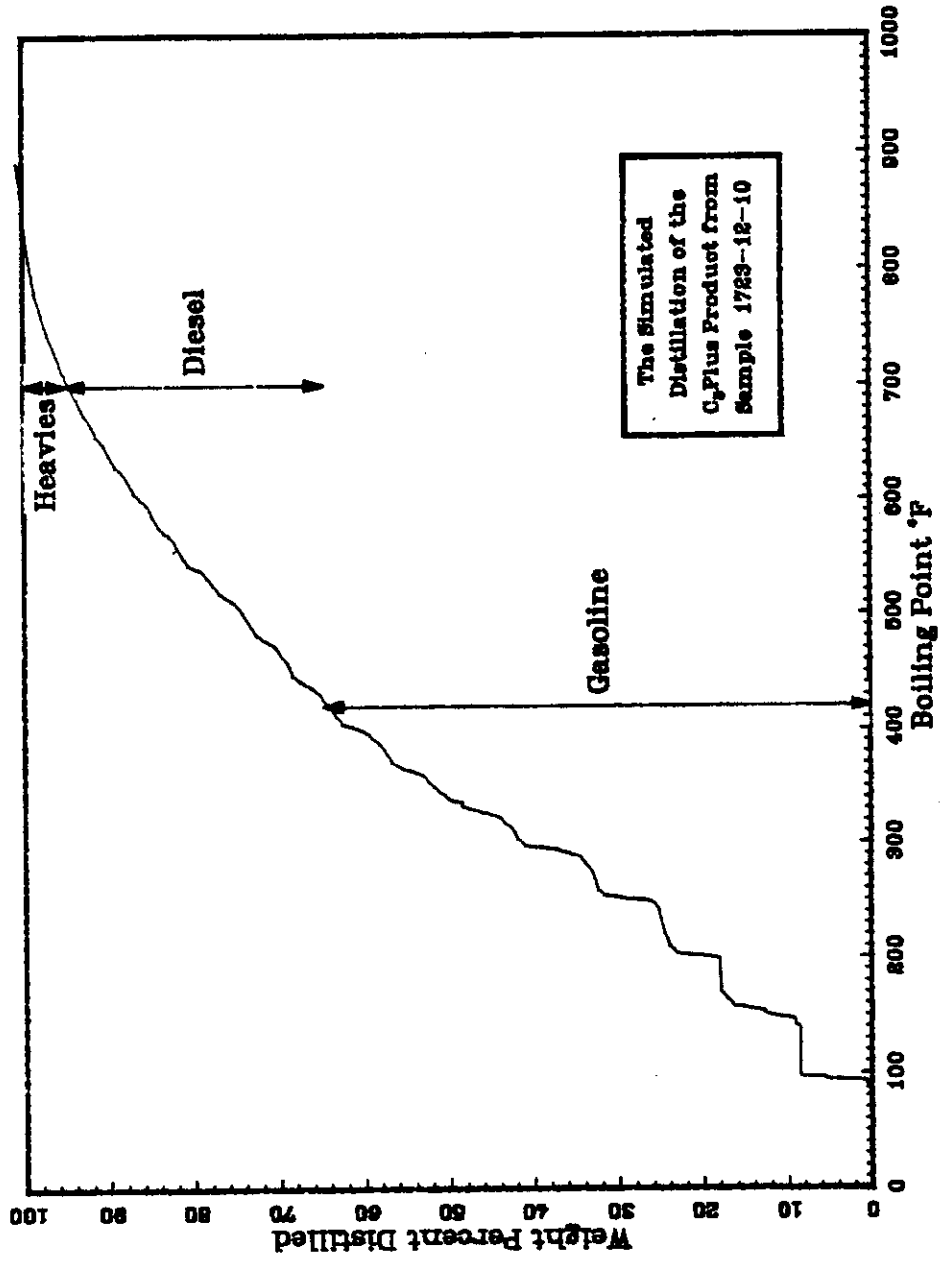


Fig. 94

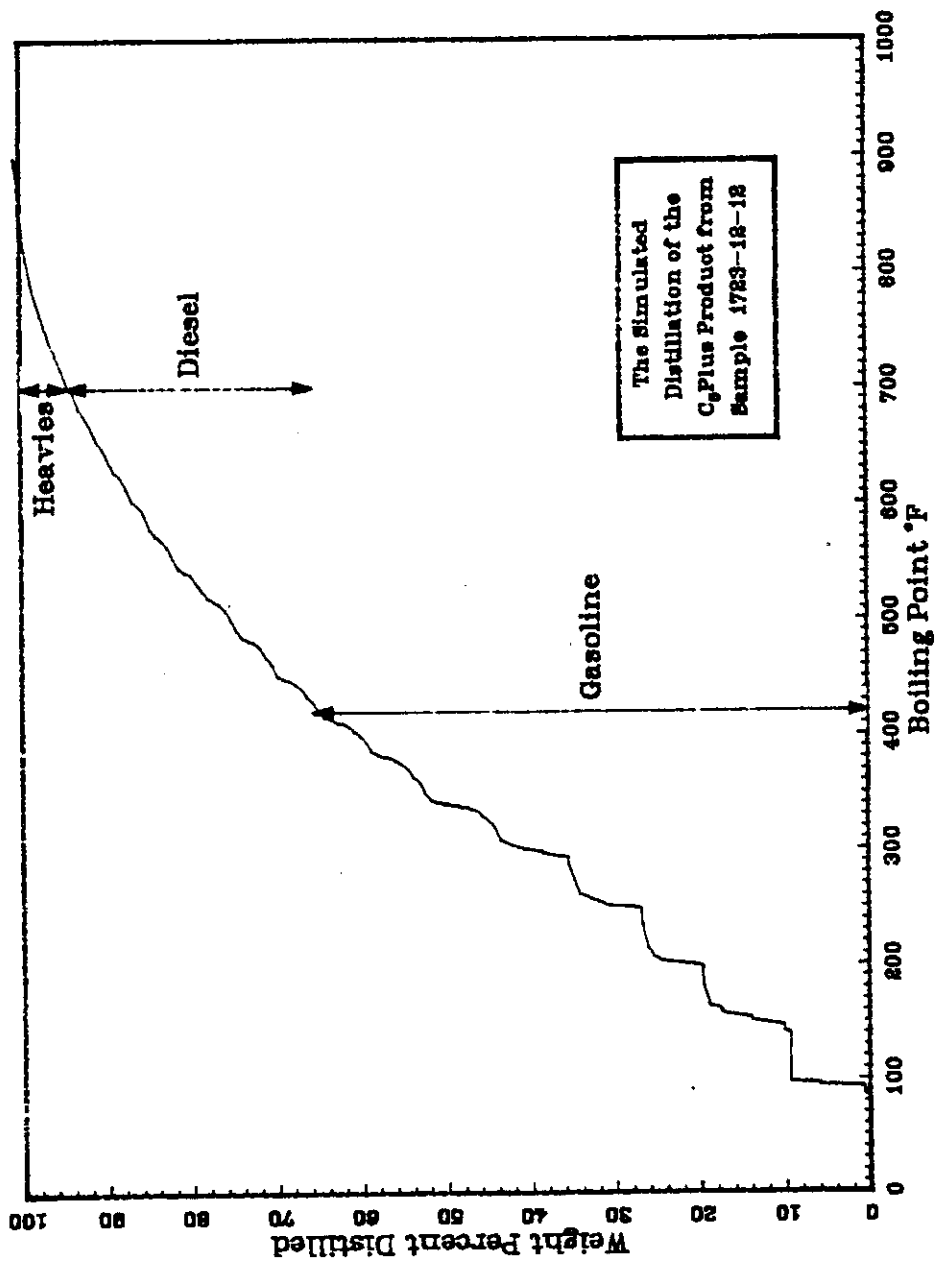


Fig. 95

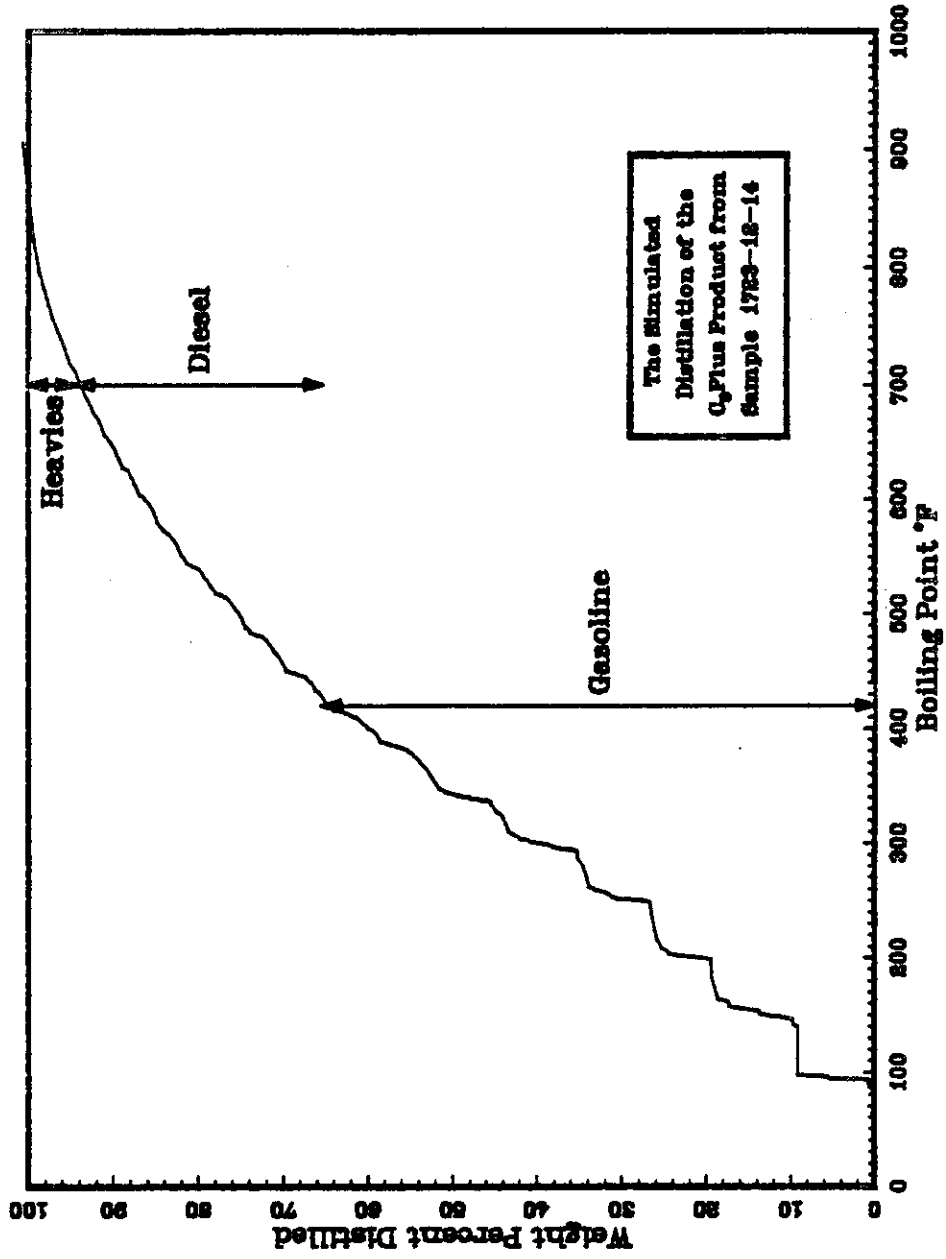


Fig. 96

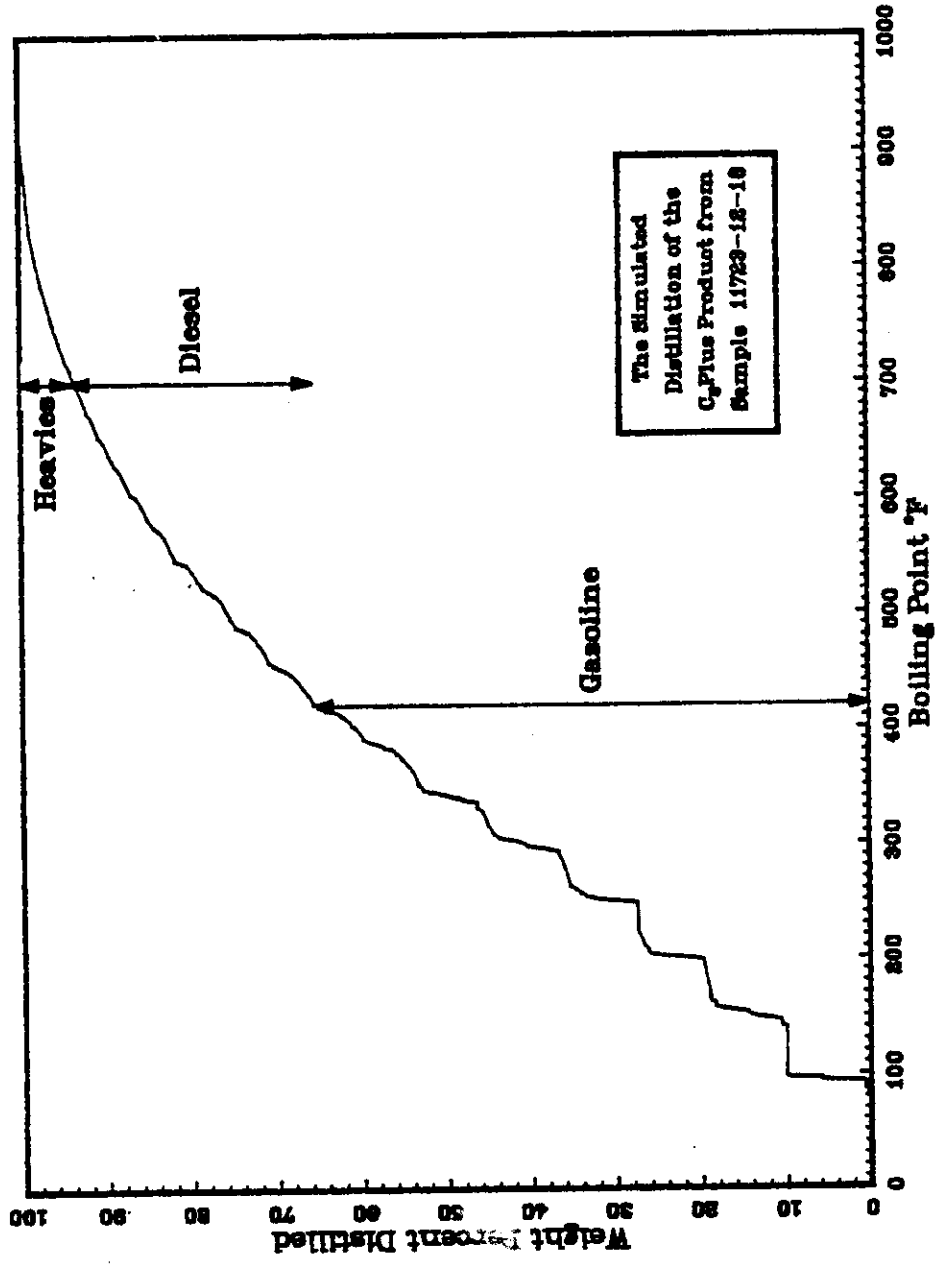


Fig. 97

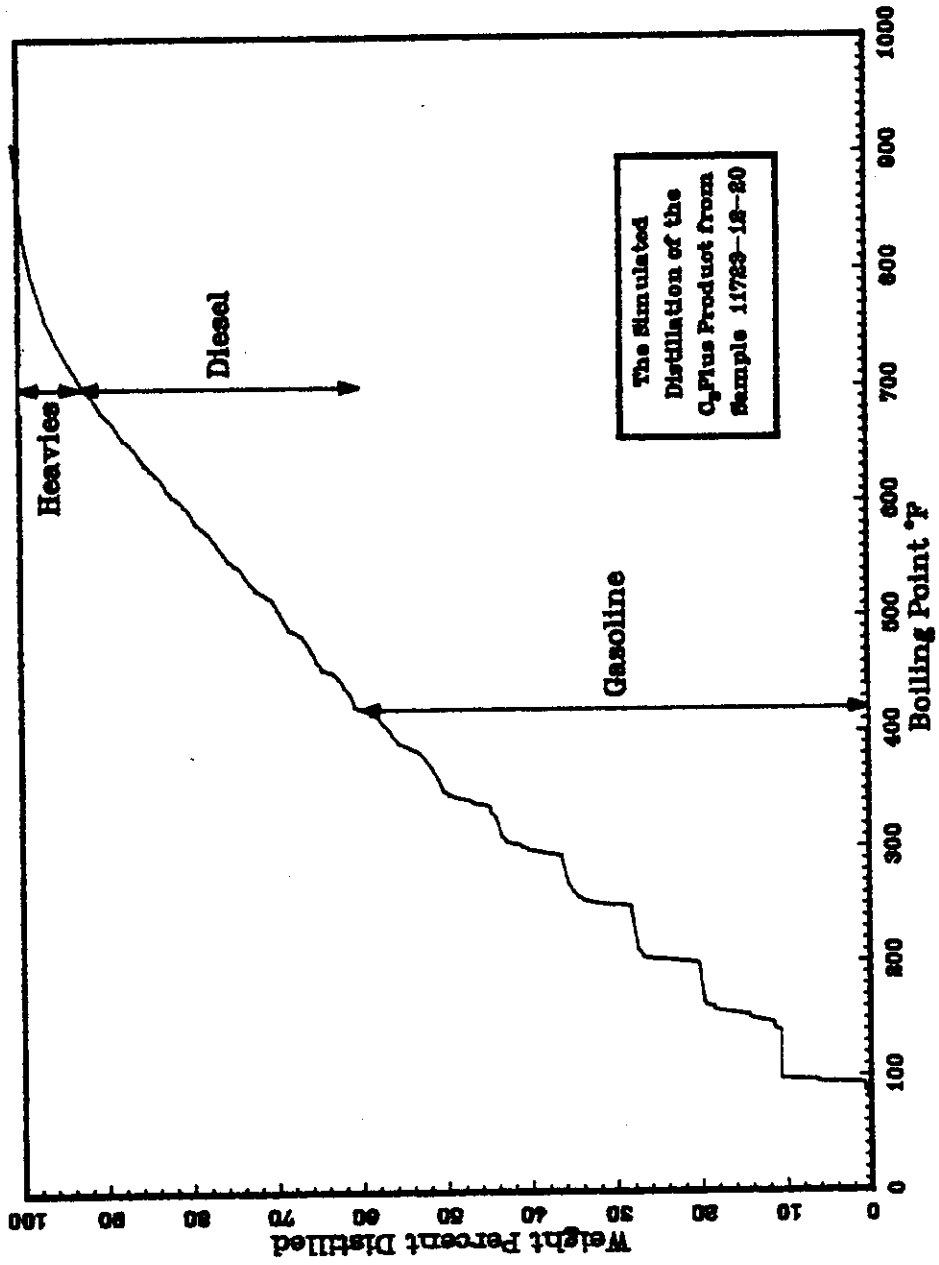


Fig. 98

