

Fig. A87

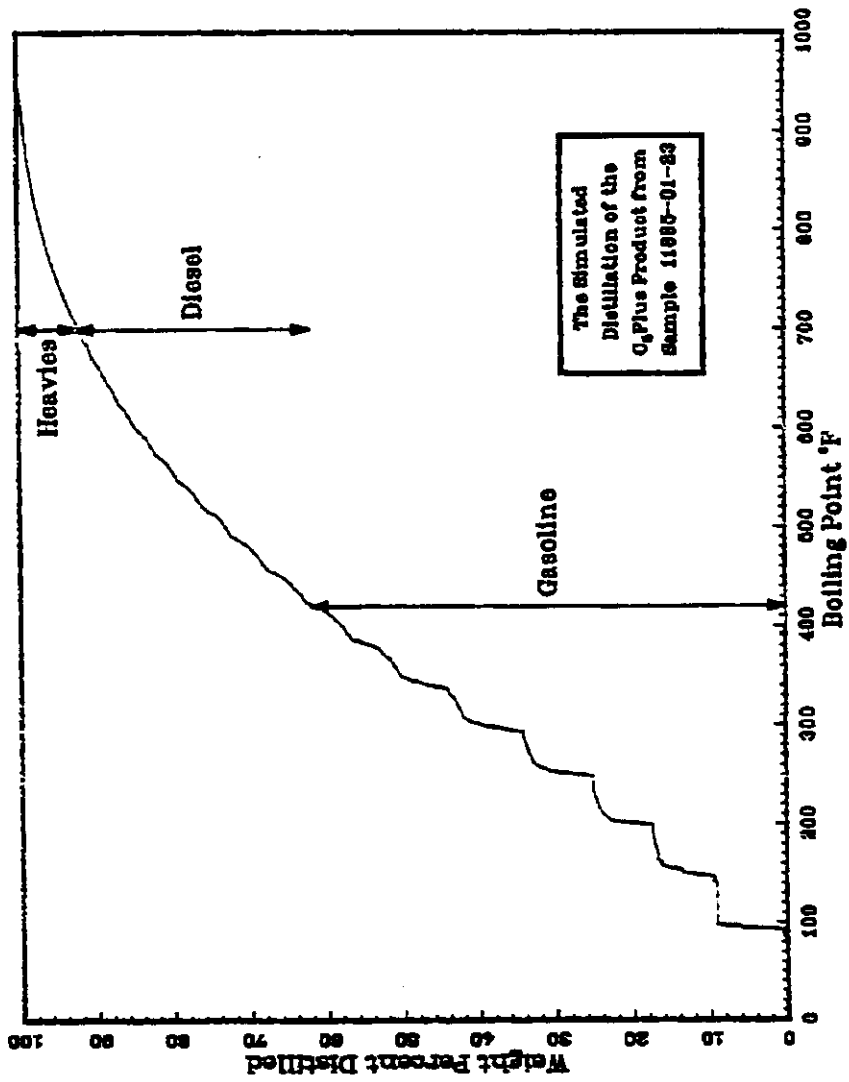


Fig. A88

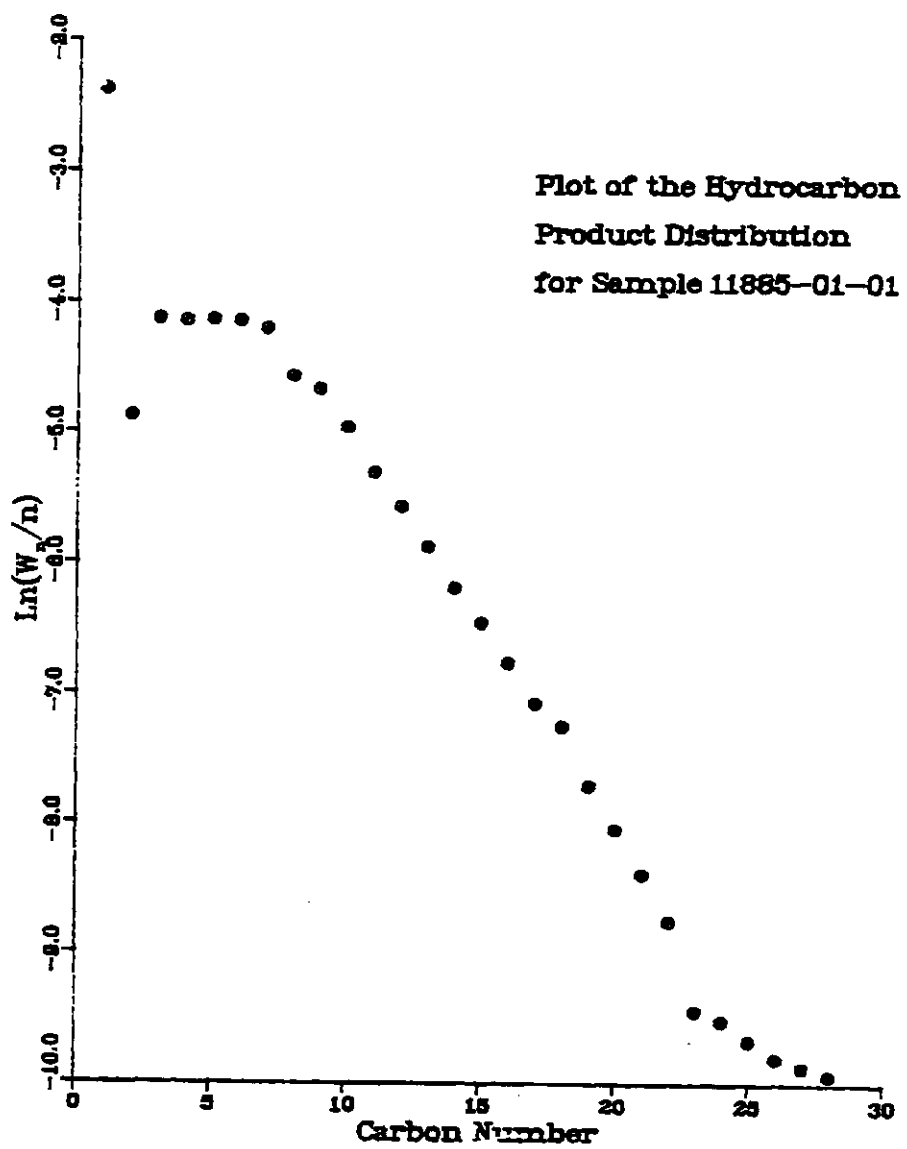


Fig. A89

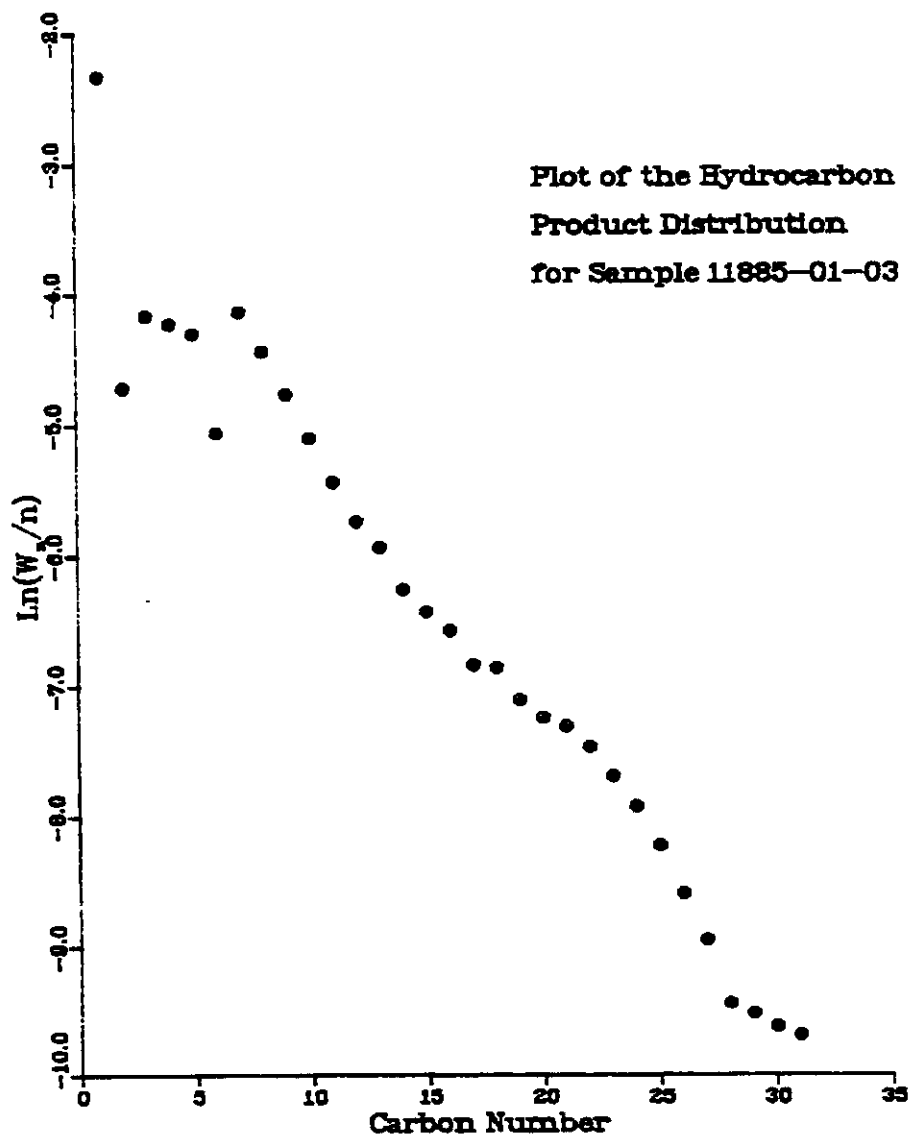


Fig. A90

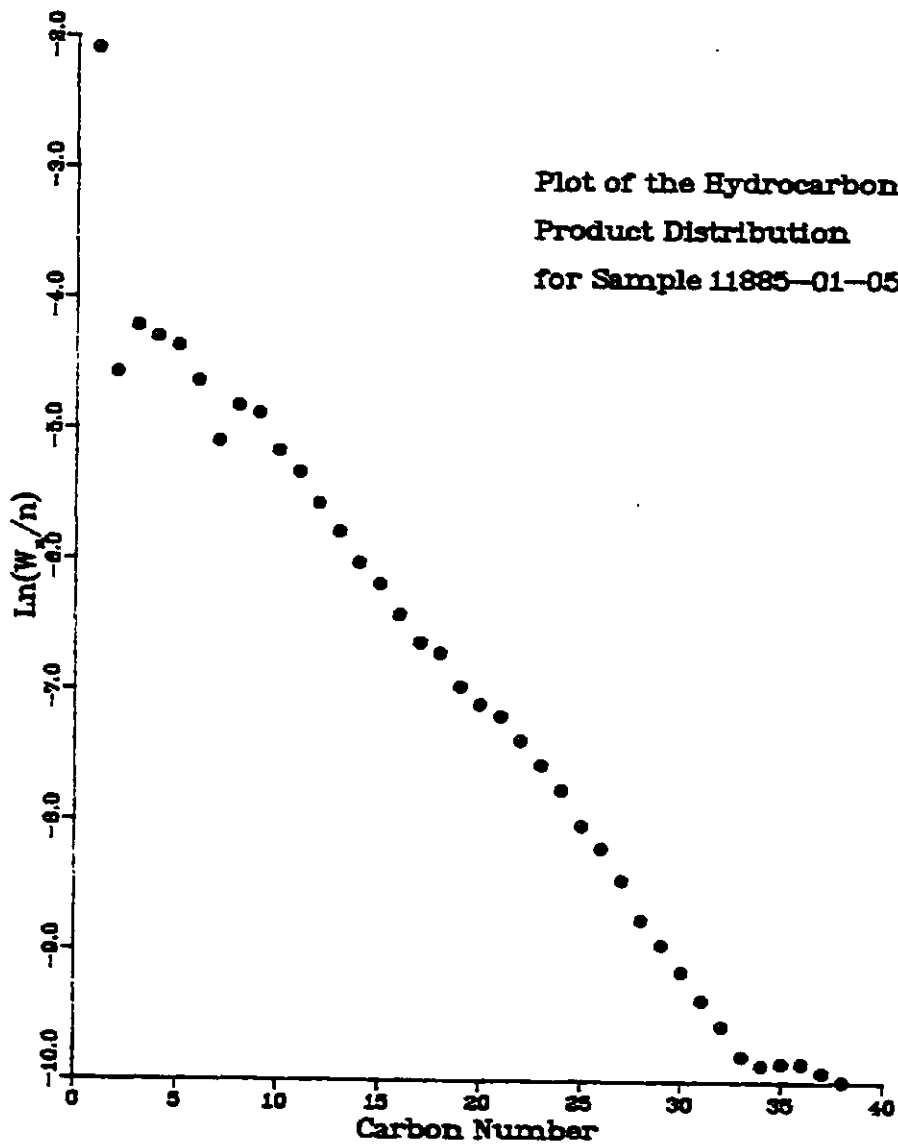


Fig. A91

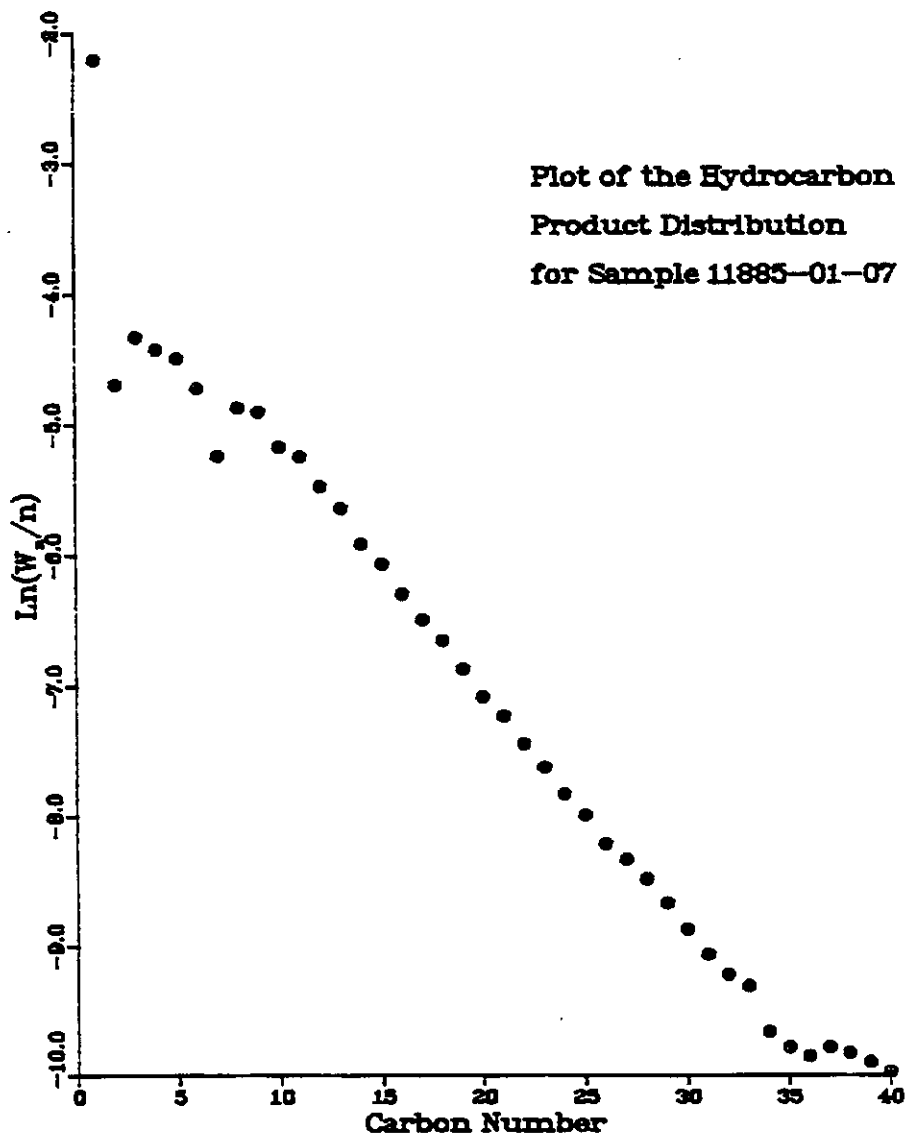


Fig. A92

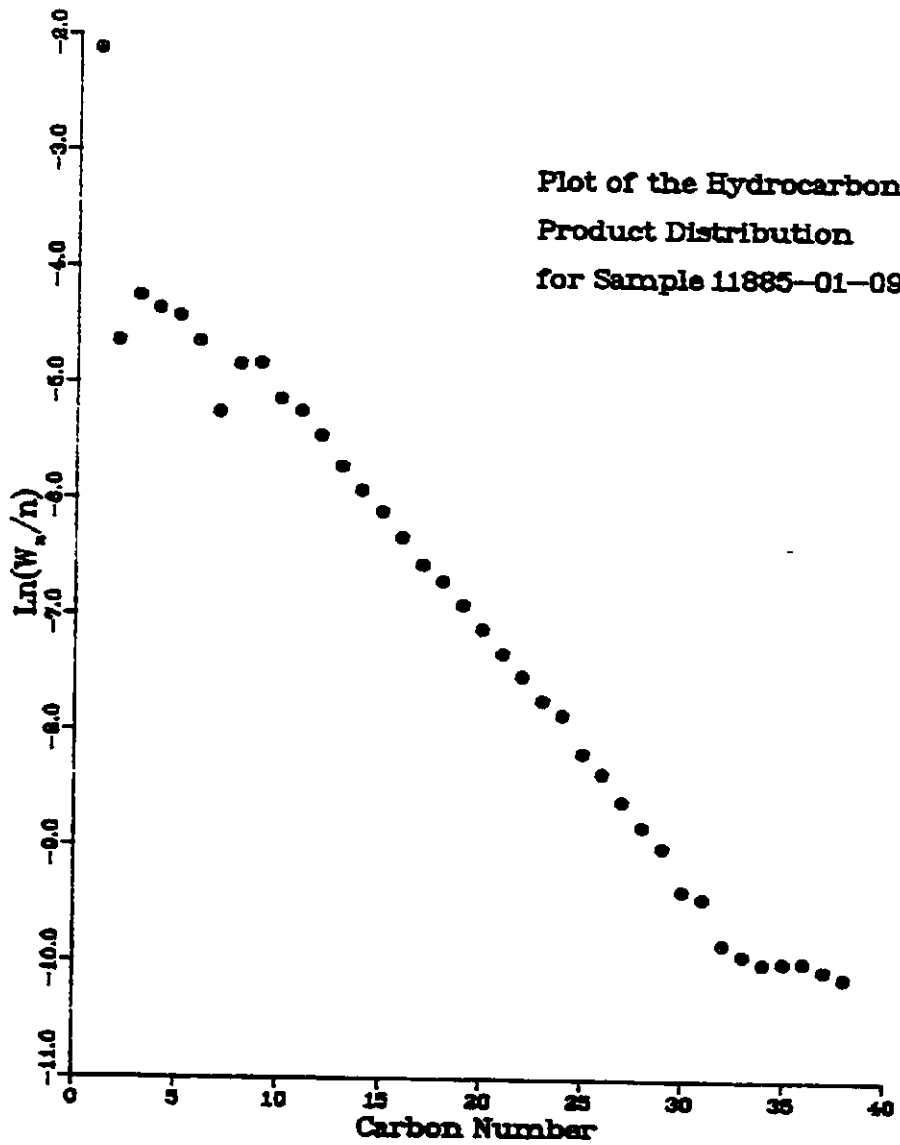


Fig. A93

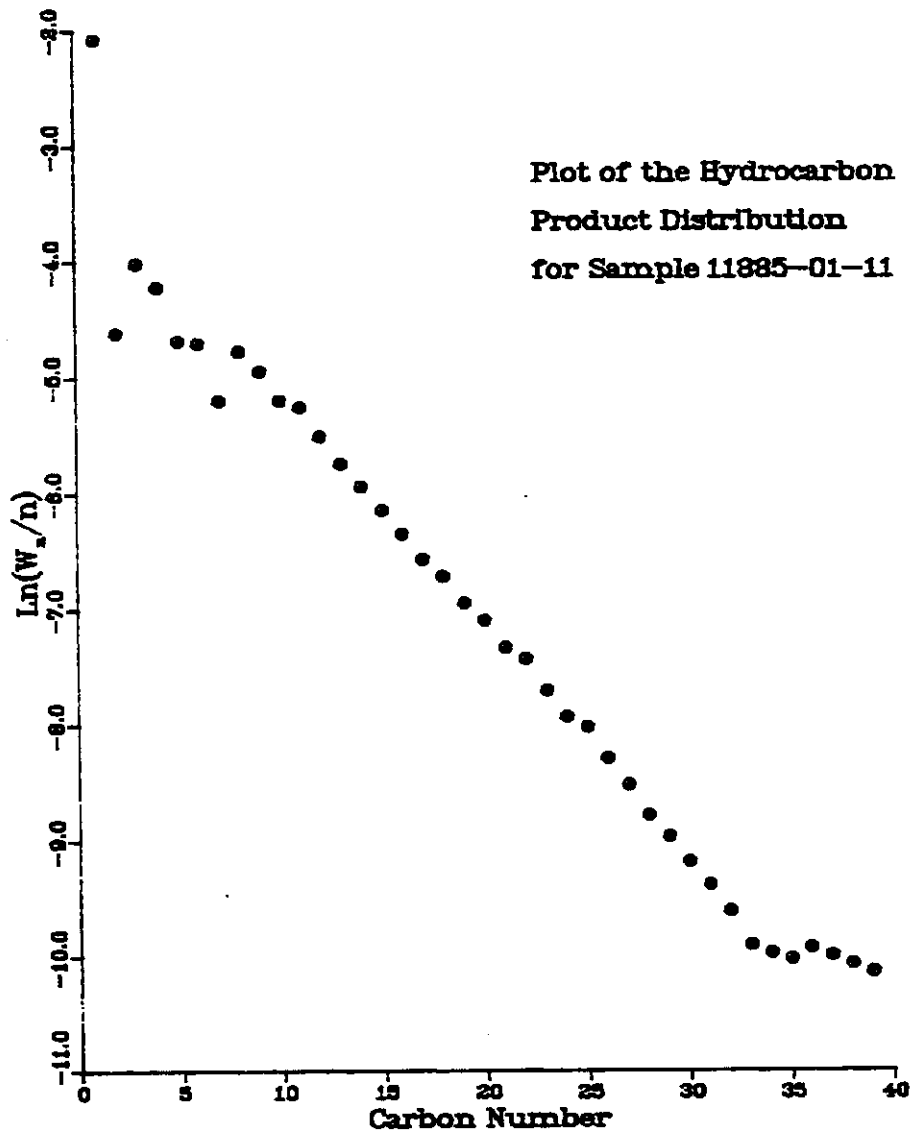


Fig. A94

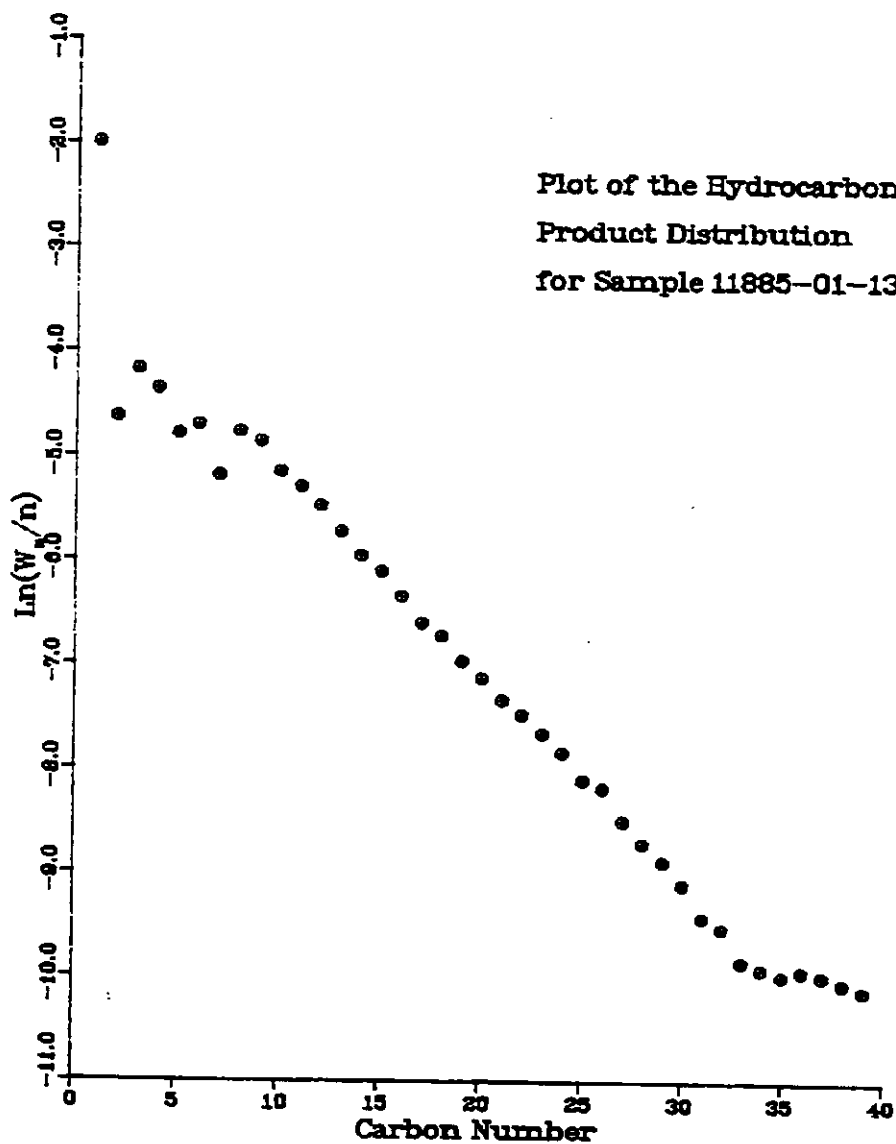


Fig. A95

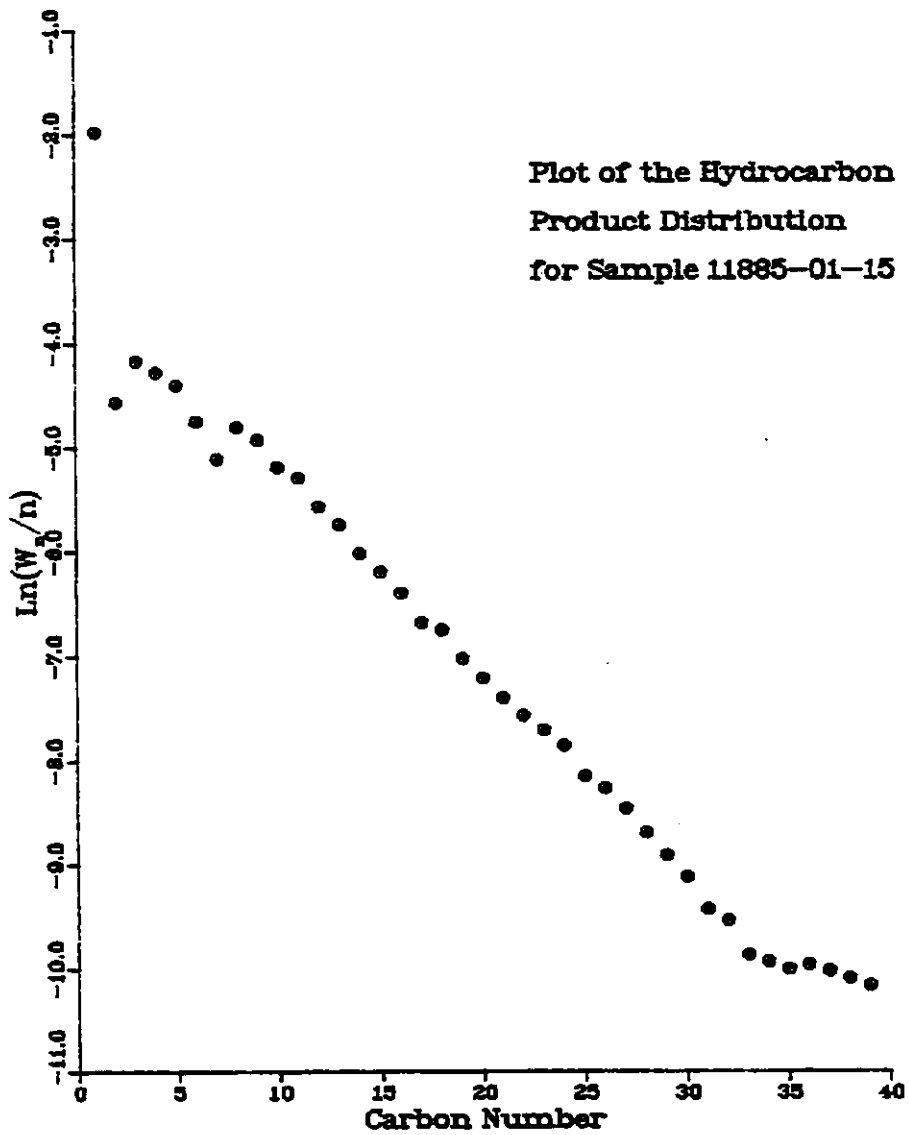


Fig. A96

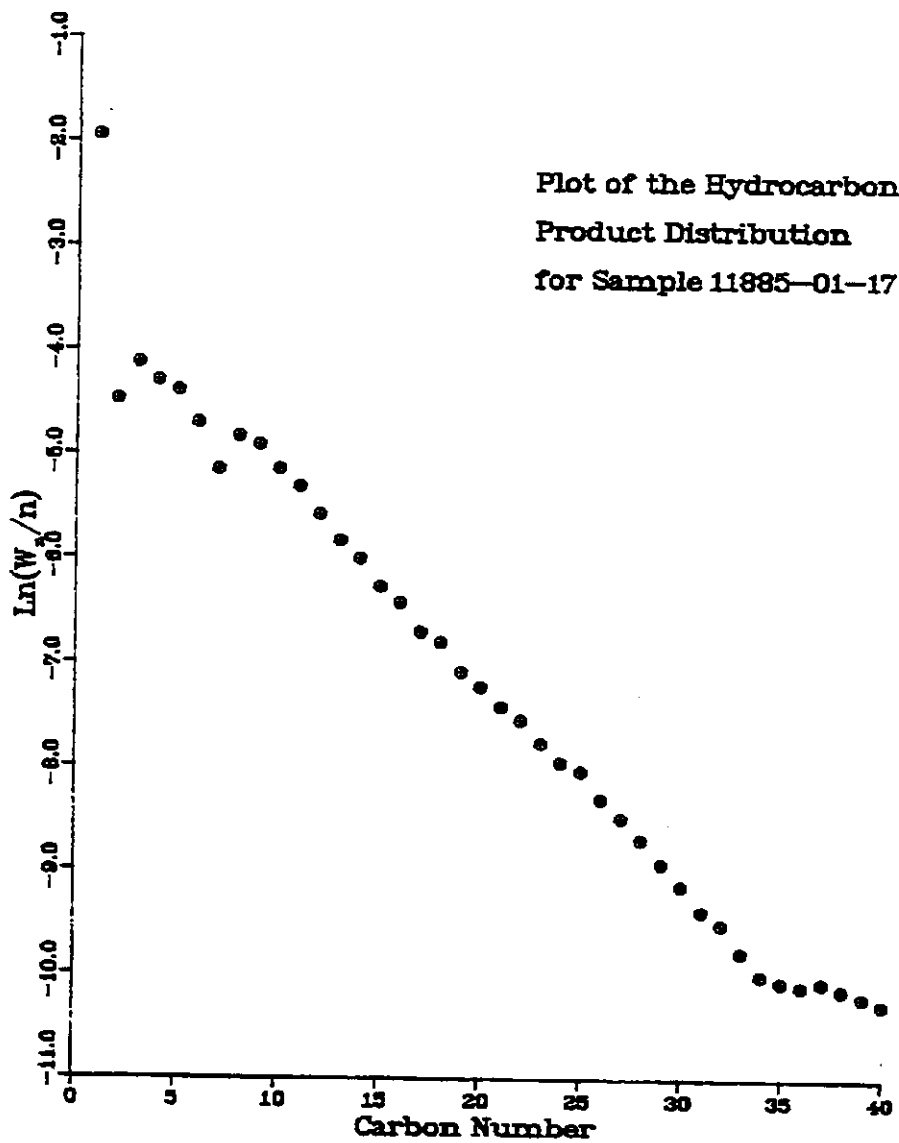


Fig. A97

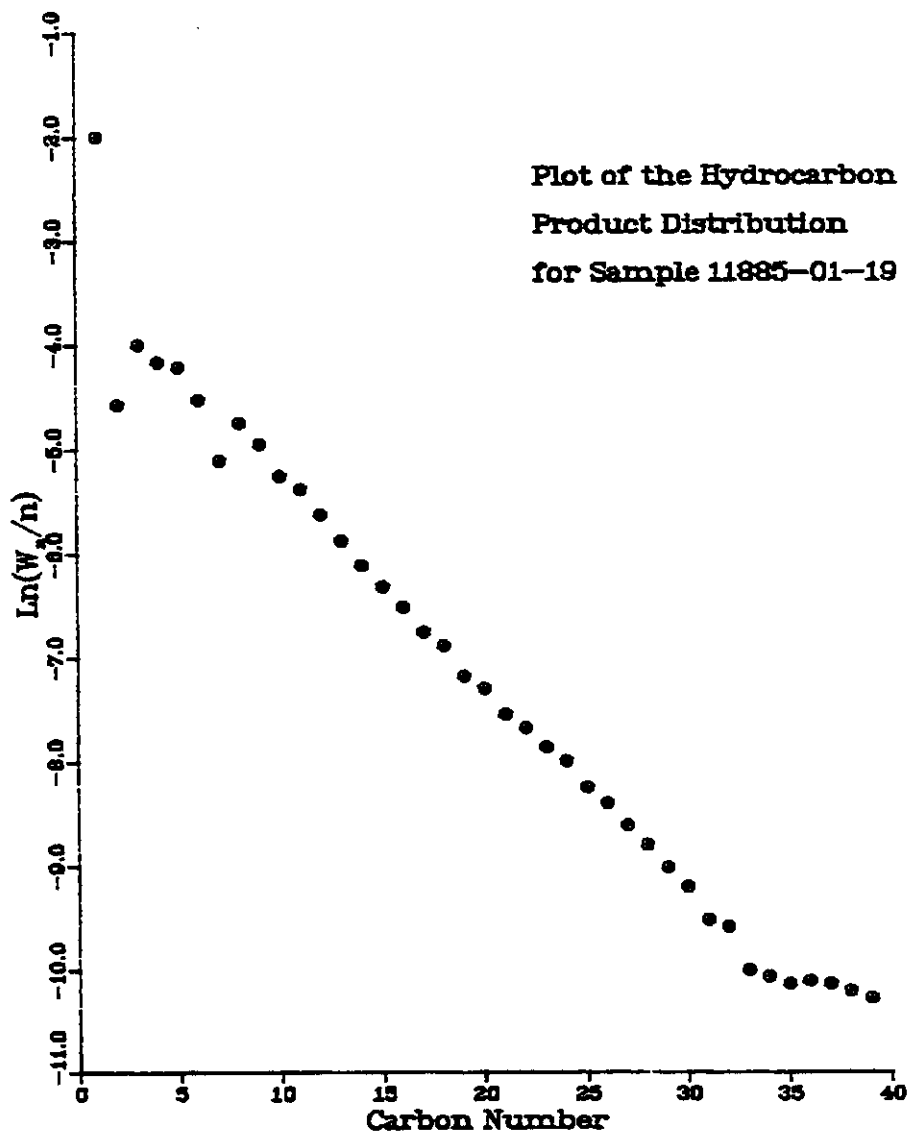


Fig. A98

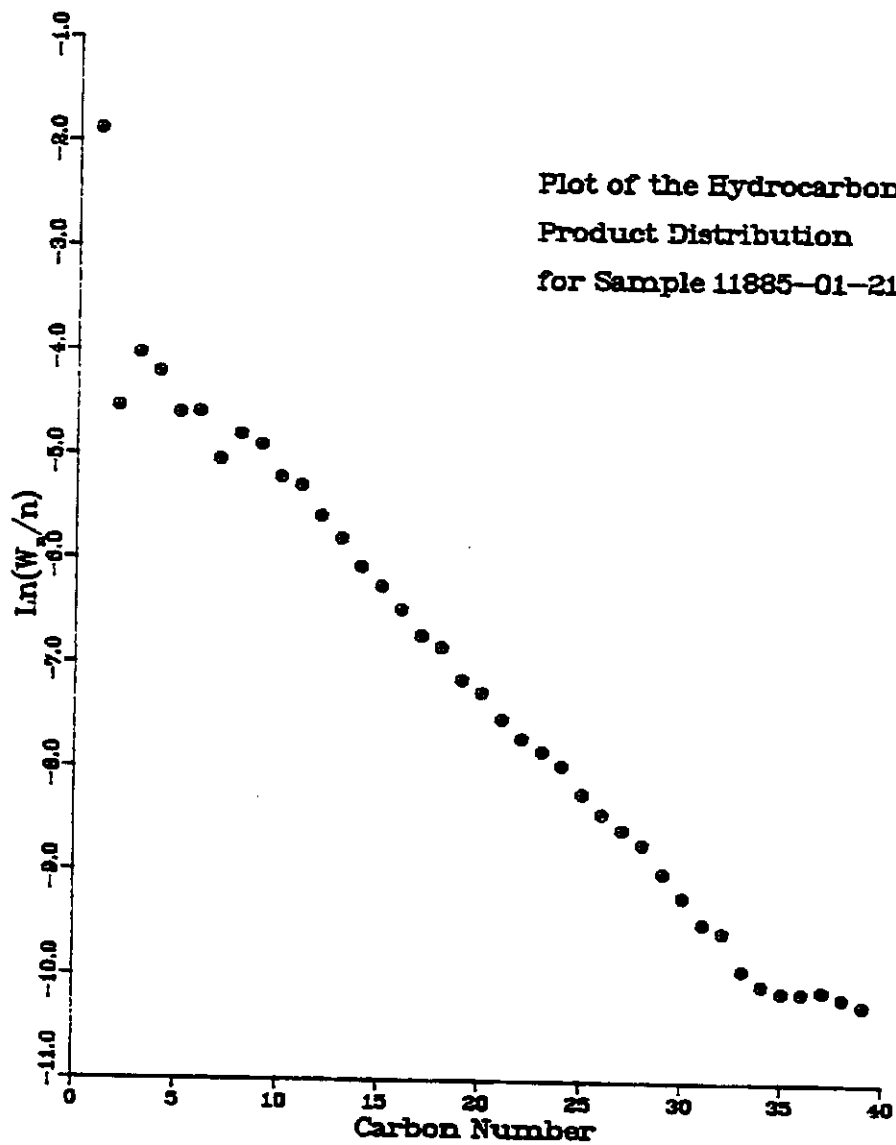


Fig. A99

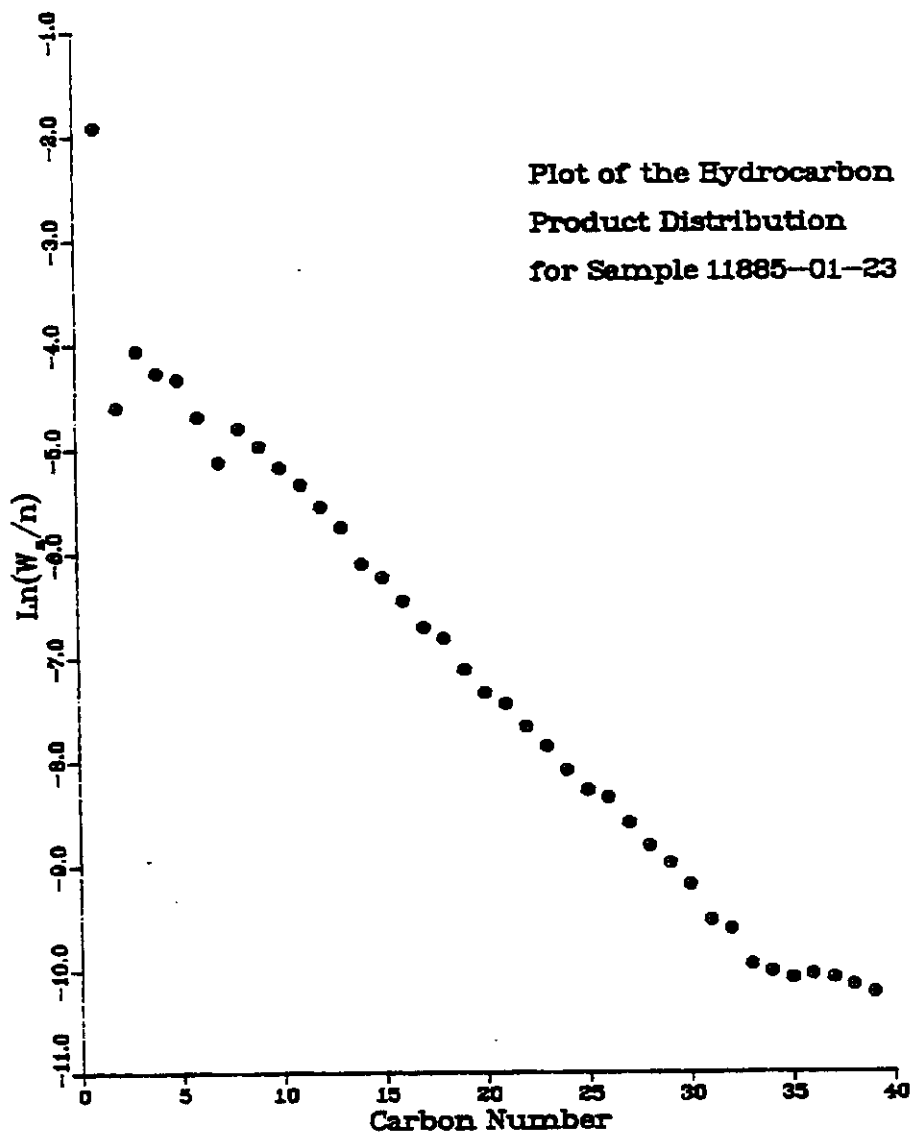
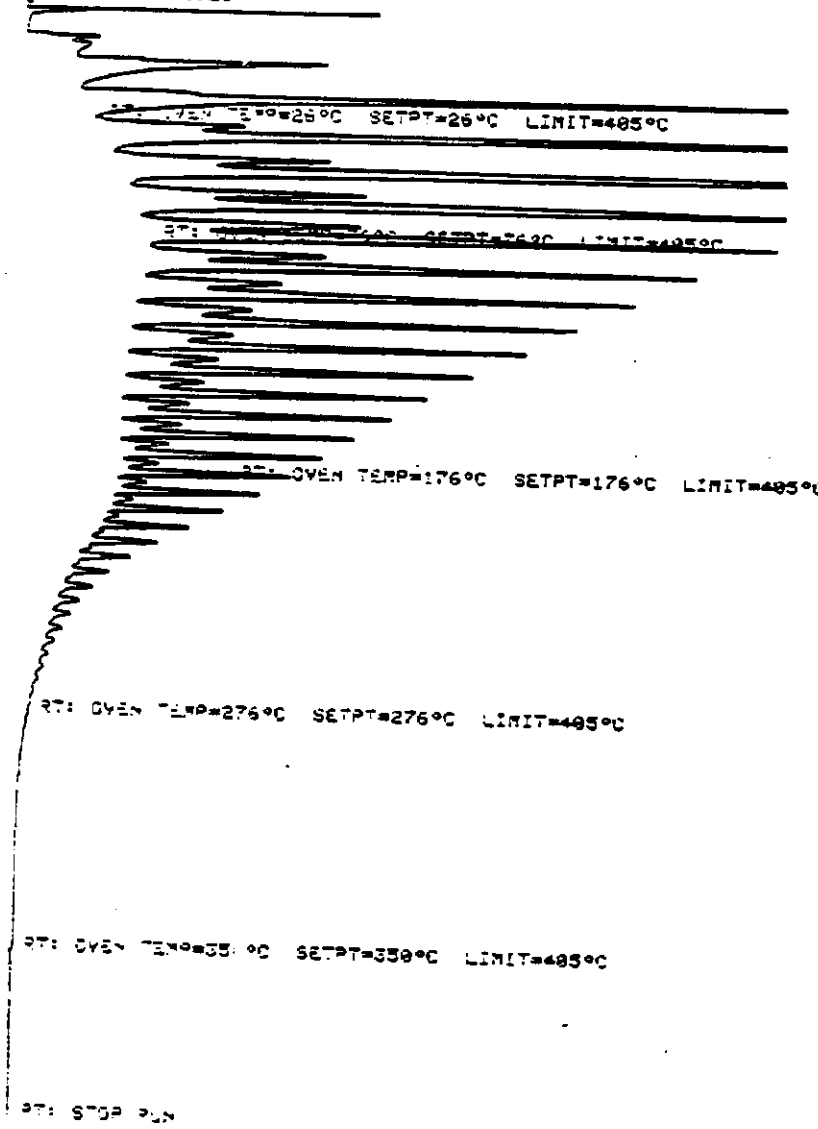


Fig. A100

OVEN TEMP NOT READY

RT: SLICES 4.29



RT: STOP RUN

Fig. A101

OVEN TEMP NOT REACH

SET POINT=25°C

SET POINT=25°C SET POINT=26°C LIMIT=405°C

SET POINT=25°C SET POINT=26°C LIMIT=405°C

SET POINT=276°C SET POINT=176°C LIMIT=405°C

SET POINT=276°C SET POINT=276°C LIMIT=405°C

SET POINT=330°C SET POINT=330°C LIMIT=405°C

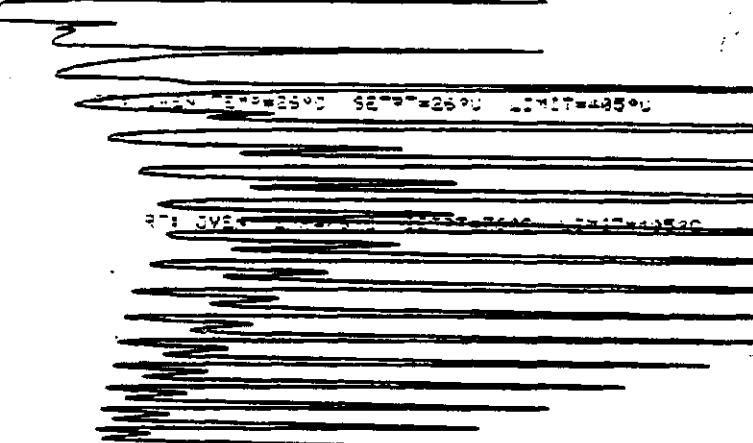
SET POINT=...

SET POINT=...

Fig. A102

1000 1000 1000 1000

1000 1000 1000 1000



1000 1000 1000 1000

1000 1000 1000 1000

1000 1000 1000 1000

1000 1000 1000 1000

1000 1000 1000 1000

1000 1000 1000 1000

1000 1000 1000 1000

Fig. A103

Table All

RESULT OF SYNGAS OPERATION

RUN NO. 11885-01
 CATALYST Co/Th/X4-U103+U101 11864-13C 250 CC 117.7G(161.3 @END +43.6G)
 FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-01-01	885-01-03	885-01-05	885-01-07	885-01-09
FEED H2:CO:AR	49:50: 0	49:50: 0	49:50: 0	49:50: 0	49:50: 0
HRS ON STREAM	20.0	44.5	69.5	93.0	116.5
PRESSURE, PSIG	297	295	293	300	299
TEMP. C	263	262	263	262	262
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	20.00	24.50	25.00	23.50	23.50
EFFLNT GAS LITER	336.45	778.55	818.35	801.10	824.15
GM AQUEOUS LAYER	162.33	250.23	246.10	229.63	221.61
GM OIL	59.51	76.37	92.08	109.88	97.10
MATERIAL BALANCE					
GM ATOM CARBON %	57.83	90.44	90.16	96.19	94.64
GM ATOM HYDROGEN %	72.82	94.36	92.95	99.41	98.40
GM ATOM OXYGEN %	62.73	99.13	99.20	100.44	99.55
RATIO CHX/(H2O+CO2)	0.8534	0.7892	0.7720	0.8918	0.8711
RATIO X IN CHX	2.2944	2.2740	2.3403	2.3179	2.3354
USAGE H2/CO PRODT	1.9020	2.0480	2.1137	2.0049	2.0255
FEED H2/CO FRM EFFLNT	1.2201	1.0109	0.9989	1.0013	1.0074
RESIDUAL H2/CO RATIO	0.3359	0.3135	0.3215	0.3407	0.3734
RATIO CO2/(H2O+CO2)	0.1226	0.0922	0.0872	0.0818	0.0836
K SHIFT IN EFFLNT	0.0469	0.0318	0.0307	0.0303	0.0341
SPECIFIC ACTIVITY SA	4.4092	3.0314	2.5468	2.5777	2.1554
CONVERSION					
ON CO %	56.46	40.21	37.80	39.70	38.37
ON H2 %	88.01	81.46	79.98	79.48	77.16
ON CO+H2 %	73.80	60.95	58.88	59.60	57.84
PRDT SELECTIVITY, WT %					
CH4	9.29	9.71	12.39	11.03	12.02
C2 HC'S	1.52	1.79	2.06	1.83	1.93
C3H8	2.16	1.83	1.95	1.81	2.02
C3H6=	2.65	2.84	2.46	2.16	2.25
C4H10	2.47	1.57	1.65	1.48	1.62
C4H8=	3.85	4.25	3.77	3.34	3.50
C5H12	3.65	1.71	1.58	1.46	1.64
C5H10=	4.52	5.06	4.76	4.16	4.35
C6H14	5.06	1.80	1.92	1.74	1.94
C6H12= & CYCLO'S	3.20	2.03	3.89	3.63	3.85
C7+ IN GAS	15.78	25.04	10.59	8.39	9.95
LIQ HC'S	46.06	42.36	52.98	58.97	54.93
TOTAL	100.00	100.00	100.00	100.00	100.00

Table All (continued)

SUB-GROUPING					
C1 -C4	21.94	21.99	24.27	21.65	23.33
C5 -420 F	61.25	53.72	45.13	43.95	45.63
420-700 F	15.94	20.32	23.95	26.64	25.14
700-END PT	0.87	3.97	6.65	7.75	5.89
C5+-END PT	78.06	78.01	75.73	78.35	76.67
ISO/NORMAL MOLE RATIO					
C4	0.1485	0.0721	0.0738	0.0540	0.0562
C5	0.2153	0.1534	0.0627	0.0505	0.0522
C6	0.3586	0.2673	0.2033	0.1744	0.1628
C4=	0.0527	0.0450	0.0492	0.0479	0.0495
PARAFFIN/OLEFIN RATIO					
C3	0.7781	0.6134	0.7560	0.8003	0.8593
C4	0.6189	0.3570	0.4230	0.4293	0.4457
C5	0.8218	0.3289	0.3236	0.3406	0.3668
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7600	0.8213	0.8327	0.8379	0.8277
RATIO CH4/(1-A)**2	1.6122	3.0405	4.4281	4.1978	4.0495
ALPHA FRM CORRELATION					
ALPHA (EXPTL/CORR)	0.8638	0.8672	0.8659	0.8631	0.8587
	0.8799	0.9471	0.9617	0.9707	0.9640
W%CH4 FRM CORRELATION					
W%CH4 (EXPTL/CORR)	10.7011	9.4299	10.0360	10.6902	12.0758
	0.8677	1.0298	1.2343	1.0320	0.9950
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	CLDY OIL	CLDY OIL	CLDY OIL	CLDY/SLD
DENSITY	0.7424	0.7636	0.755	0.752	0.745
N, REFRACTIVE INDEX	1.4180	1.4296	1.4306	1.4310	1.4296
SIMULT'D DISTILATN					
10 WT % @ DEG F	213	266	275	276	280
16	253	303	303	303	303
50	370	453	456	456	451
84	525	652	669	670	649
90	573	695	725	736	708
RANGE(16-84 %)	272	349	366	367	346
WT % @ 420 F	63.50	42.67	42.25	41.67	43.50
WT % @ 700 F	98.12	90.63	87.45	86.85	89.27

NEW FORMAT JAN 25,85

Table A12

RESULT OF SYNGAS OPERATION

RUN NO. 11885-01
 CATALYST Co/Th/X4-U103+U101 11864-13C 250 CC 117.7G(161.3 @END +43.6G)
 FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-01-11	885-01-13	885-01-15	885-01-17	885-01-19
FEED H2:CO:AR	49:50: 0	49:50: 0	49:50: 0	49:50: 0	49:50: 0
HRS ON STREAM	140.0	163.0	187.5	211.5	235.5
PRESSURE,PSIG	297	299	299	298	298
TEMP. C	263	263	263	263	264
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	23.53	23.47	24.00	24.00	24.00
EFFLNT GAS LITER	854.85	876.60	919.25	938.70	943.00
GM AQUEOUS LAYER	217.17	212.48	213.93	208.19	207.13
GM OIL	101.31	96.95	93.27	88.51	88.71
MATERIAL BALANCE					
GM ATOM CARBON %	97.04	96.51	96.70	97.06	99.24
GM ATOM HYDROGEN %	101.68	100.54	101.19	101.14	103.74
GM ATOM OXYGEN %	100.03	100.90	100.95	100.89	100.76
RATIO CHX/(H2O+CO2)	0.9205	0.8816	0.8835	0.8924	0.9576
RATIO X IN CHX	2.3515	2.3697	2.3720	2.3813	2.3685
USAGE H2/CO PRODT	1.9699	2.0045	2.0127	2.0068	1.9360
FEED H2/CO FRM EFFLNT	1.0152	1.0093	1.0139	1.0096	1.0128
RESIDUAL H2/CO RATIO	0.3996	0.4142	0.4348	0.4468	0.4508
RATIO CO2/(H2O+CO2)	0.0906	0.0923	0.0895	0.0904	0.0954
K SHIFT IN EFFLNT	0.0398	0.0421	0.0427	0.0444	0.0475
SPECIFIC ACTIVITY SA	1.9225	1.6960	1.5415	1.4532	1.4566
CONVERSION					
ON CO %	39.20	37.42	36.70	36.08	37.84
ON H2 %	76.07	74.32	72.86	71.71	72.34
ON CO+H2 %	57.77	55.96	54.90	53.98	55.20
PRDT SELECTIVITY,WT %					
CH4	12.51	13.59	13.85	14.34	13.58
C2 HC'S	1.97	1.95	2.08	2.26	2.07
C3H8	2.32	2.20	2.24	2.43	2.73
C3H6=	3.10	2.41	2.39	2.43	2.78
C4H10	2.02	1.75	1.87	1.84	2.17
C4H8=	3.87	3.35	3.68	3.60	4.07
C5H12	2.22	1.87	1.89	1.96	2.20
C5H10=	2.40	2.27	4.25	4.24	5.20
C6H14	2.03	1.96	1.88	1.99	2.44
C6H12= & CYCLO'S	3.39	3.49	3.29	3.43	4.05
C7+ IN GAS	9.45	9.62	9.60	10.54	11.14
LIQ HC'S	54.70	55.54	52.99	50.94	47.57
TOTAL	100.00	100.00	100.00	100.00	100.00

Table A12 (continued)

SUB-GROUPING					
C1 -C4	25.80	25.25	26.10	26.91	27.39
C5 -420 F	43.02	43.46	44.05	44.40	46.09
420-700 F	24.89	24.73	23.45	22.33	20.81
700-END PT	6.29	6.55	6.40	6.37	5.71
C5+-END PT	74.20	74.75	73.90	73.09	72.61
ISO/NORMAL MOLE RATIO					
C4	0.0435	0.0580	0.0468	0.0496	0.0510
C5	0.0931	0.0618	0.0931	0.0617	0.0644
C6	0.2632	0.2038	0.1468	0.1413	0.1942
C4=	0.0706	0.0529	0.0578	0.0564	0.0577
PARAFFIN/OLEFIN RATIO					
C3	0.7134	0.8703	0.8931	0.9545	0.9384
C4	0.5039	0.5040	0.4905	0.4934	0.5146
C5	0.8976	0.8006	0.4324	0.4507	0.4116
SCHULZ-FLORY DISTRTBN					
ALPHA (EXP(SLOPE))	0.8307	0.8336	0.8306	0.8288	0.8202
RATIO CH4/(1-A)**2	4.3662	4.9076	4.8250	4.8907	4.2027
ALPHA FRM CORRELATION					
ALPHA (EXPTL/CORR)	0.8553	0.8536	0.8512	0.8499	0.8494
	0.9712	0.9766	0.9758	0.9752	0.9657
W%CH4 FRM CORRELATION					
W%CH4 (EXPTL/CORR)	13.3258	13.8690	14.6003	15.0109	15.3702
	0.9389	0.9800	0.9484	0.9552	0.8835
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY/SLD	CLDY/SLD	CLDY/SLD	CLDY/SLD	CLDY/SLD
DENSITY	0.760	0.760	0.774	0.759	0.761
N, REFRACTIVE INDEX	1.430	1.4290	1.4293	1.4290	1.4290
SIMULT'D DISTILATN					
10 WT % @ DEG F	274	272	269	280	270
16	302	302	302	303	302
50	453	451	451	452	450
84	660	661	663	666	661
90	716	720	723	727	723
RANGE(16-84 %)	358	359	361	363	359
WT % @ 420 F	43.00	43.67	43.67	43.67	44.25
WT % @ 700 F	88.50	88.20	87.92	87.50	88.00

NEW FORMAT JAN 25,85

Table A13

RESULT OF SYNGAS OPERATION

RUN NO. 11885-01
 CATALYST Co/Th/X4-U103-U101 11864-13C 250 CC 117.7G(161.3 @END +43.6G)
 FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11885-01-21	885-01-23
FEED H2:CO:AR	49:50: 0	49:50: 0
HRS ON STREAM	259.5	283.5
PRESSURE, PSIG	299	300
TEMP. C	264	261
FEED CC/MIN	1260	1260
HOURS FEEDING	24.00	24.00
EFFLNT GAS LITER	948.60	983.85
GM AQUEOUS LAYER	204.46	197.20
GM OIL	83.89	80.39
MATERIAL BALANCE		
GM ATOM CARBON %	96.76	95.39
GM ATOM HYDROGEN %	101.30	101.31
GM ATOM OXYGEN %	100.44	99.41
RATIO CHX/(H2O+CO2)	0.8954	0.8798
RATIO X IN CHX	2.3993	2.3906
USAGE H2/CO PRODT	2.0035	2.0699
FEED H2/CO FRM EFFLNT	1.0144	1.0290
RESIDUAL H2/CO RATIO	0.4596	0.5062
RATIO CO2/(H2O+CO2)	0.0933	0.0751
K SHIFT IN EFFLNT	0.0473	0.0411
SPECIFIC ACTIVITY SA	1.3106	1.2134
CONVERSION		
ON CO %	35.93	33.44
ON H2 %	70.97	67.26
ON CO+H2 %	53.58	50.59
PRDT SELECTIVITY, WT %		
CH4	15.21	14.76
C2 HC'S	2.12	2.01
C3H8	2.66	2.57
C3H6=	2.66	2.62
C4H10	2.06	1.95
C4H8=	3.86	3.64
C5H12	2.08	2.25
C5H10=	2.91	4.32
C6H14	2.31	2.18
C6H12= & CYCLO'S	3.76	3.36
C7+ IN GAS	11.66	10.32
LIQ HC'S	48.69	50.03
TOTAL	100.00	100.00

Table A13 (continued)

SUB-GROUPING		
C1 -C4	28.59	27.55
C5 -420 F	43.98	44.60
420-700 F	21.59	22.13
700-END PT	5.84	5.72
C5+-END PT	71.41	72.45
ISO/NORMAL MOLE RATIO		
C4	0.0457	0.0429
C5	0.0675	0.0534
C6	0.1732	0.1227
C4-	0.0603	0.0525
PARAFFIN/OLEFIN RATIO		
C3	0.9545	0.9357
C4	0.5163	0.5181
C5	0.6951	0.5062
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8237	0.8233
RATIO CH4/(1-A)**2	4.8946	4.7274
ALPHA FRM CORRELATION		
ALPHA (EXPTL/CORR)	0.8484	0.8439
	0.9709	0.9756
W%CH4 FRM CORRELATION		
W%CH4 (EXPTL/CORR)	15.6651	16.4469
	0.9710	0.8974
LIQ HC COLLECTION		
PHYS. APPEARANCE	CLDY WAXY	CLDY WAXY
DENSITY	0.763	0.750
N, REFRACTIVE INDEX	1.4286	1.4290
SIMULT'D DISTILATN		
10 WT % @ DEG F	283	273
16	303	302
50	451	448
84	660	653
90	723	716
RANGE(16-84 %)	357	351
WT % @ 420 F	43.67	44.33
WT % @ 700 F	88.00	88.57

NEW FORMAT JAN 25,85

VI. Run 5 (11885-05) with Catalyst 5
(Co/Th/X₄/X₈/UCC-103+UCC-101)

This catalyst is similar to Catalyst 4 but with half the cobalt, 15 percent as much X₄ as cobalt instead of one percent, and the X₄ derived from a different source--the same source used successfully for the X₄ in Run 11677-11 (Third Annual Report Catalyst 6). As in Catalyst 4, it contained one percent as much X₈ as cobalt, and 15 percent as much thorium.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. A104-107. Simulated distillations of the C₅⁺ product are plotted in Figs. A108-110. Carbon number product distributions are plotted in Figs. A111-121. Chromatograms from simulated distillations are reproduced in Figs. A122-124. Detailed material balances appear in Tables A14-16.

At 45 hours on stream the specific activity was 1.2 as against 3.0 for Catalyst 4--40 percent lower total activity, representing a cobalt utilization rate only 80 percent as good. These effects agree with previous experience that high levels of X₄, while improving stability, often reduce activity; the catalyst of Run 11677-11, with the same cobalt content as this catalyst, had an even lower specific activity of 1.0.

This catalyst was not very stable, however, deactivating at a

rate of one percentage point every 36 hours. The H₂:CO usage ratio was 2.35:1 initially and dropped to 2.15:1, which even at the lower level is higher than usual for cobalt catalysts. The conversion of H₂, as usual, deactivated more rapidly than that of CO--one percentage point every 26 hours for H₂, every 57 hours for CO. But since the H₂ conversion rate was more than twice that of CO, the H₂:CO usage ratio remained fairly constant.

The methane production, throughout the run, was about 75 percent as much as predicted by the model. Initially 12 percent, it increased at a rate of one percentage point every 67 hours, all due to the loss of total conversion and to the changing selectivity resulting from the increasing H₂:CO ratios in the reactor.

The production of C₅⁺'s, initially rather high at more than 76 percent, decreased at a rate of one percentage point every 59 hours, most of the loss in diesel fuels at one percentage point every 68 hours. Production of heavies decreased by one percentage point every 500 hours, gasoline production remained constant throughout the run, and the product became steadily lighter with time on stream. Both the isomerization and the ratio of olefins to paraffins are typical of cobalt catalysts.

From these results it appears that X₄ and X₈ not only are not additive in effect but are actually antagonistic. The X₈ canceled the positive effects usually contributed by X₄ at the level used in this catalyst.