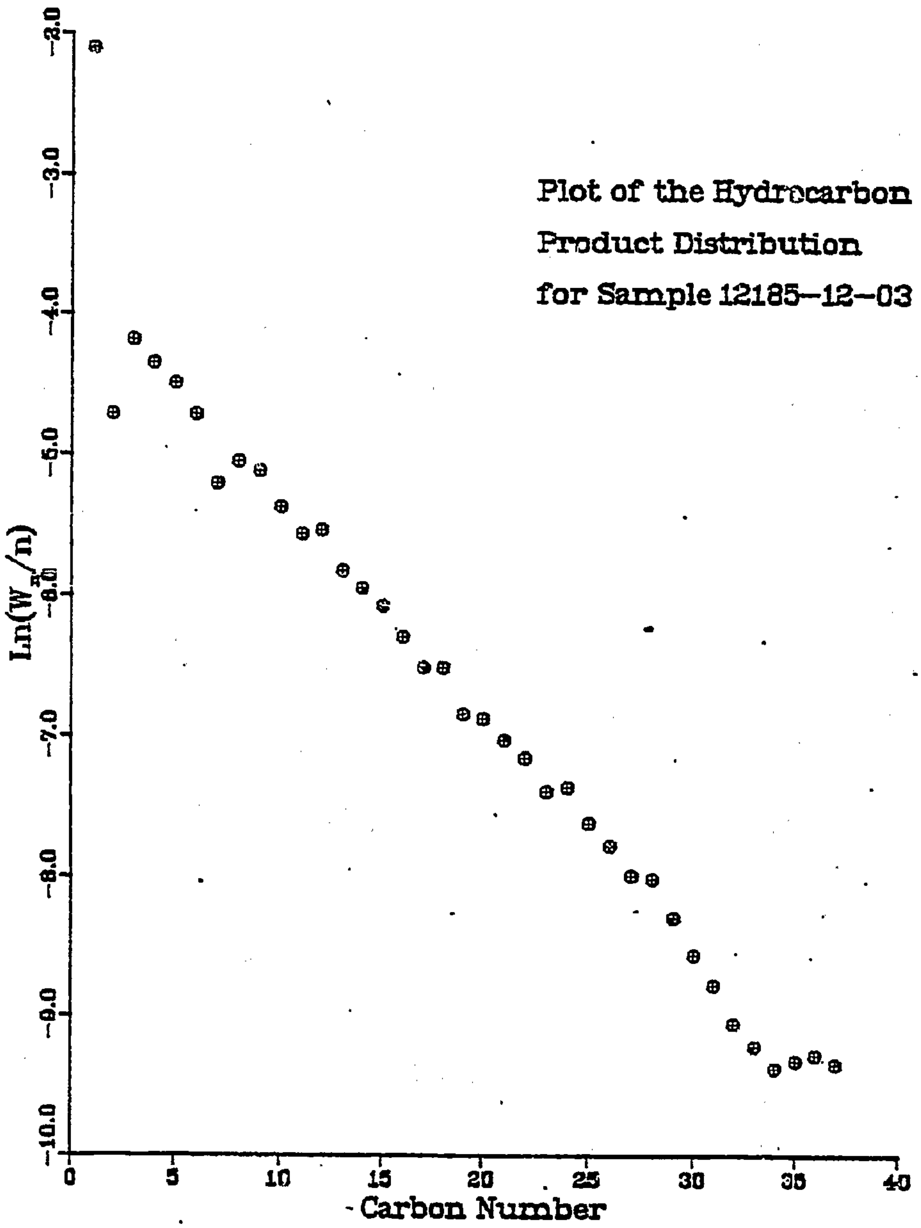

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-12-03
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B293

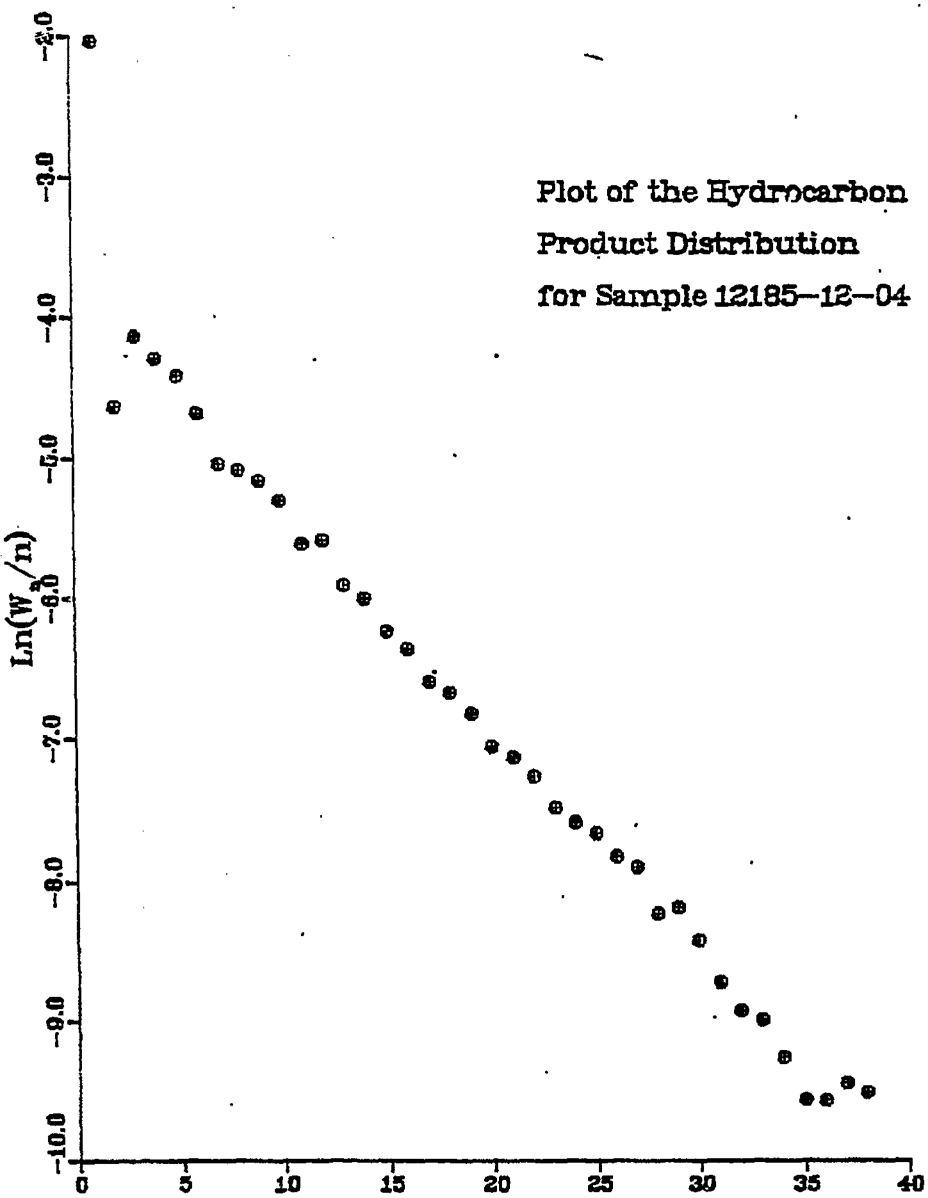

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-12-04
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B294

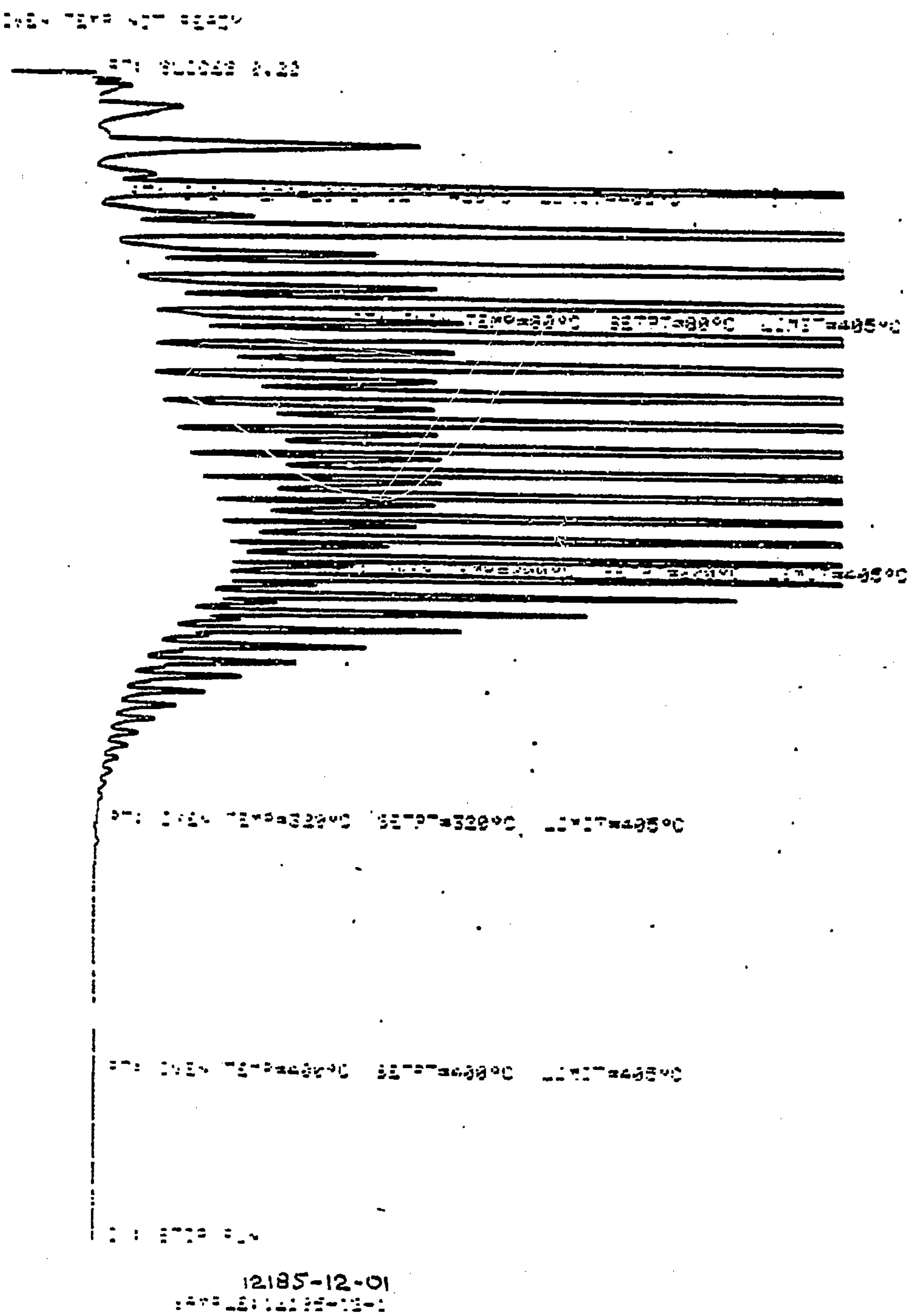


Fig. B295

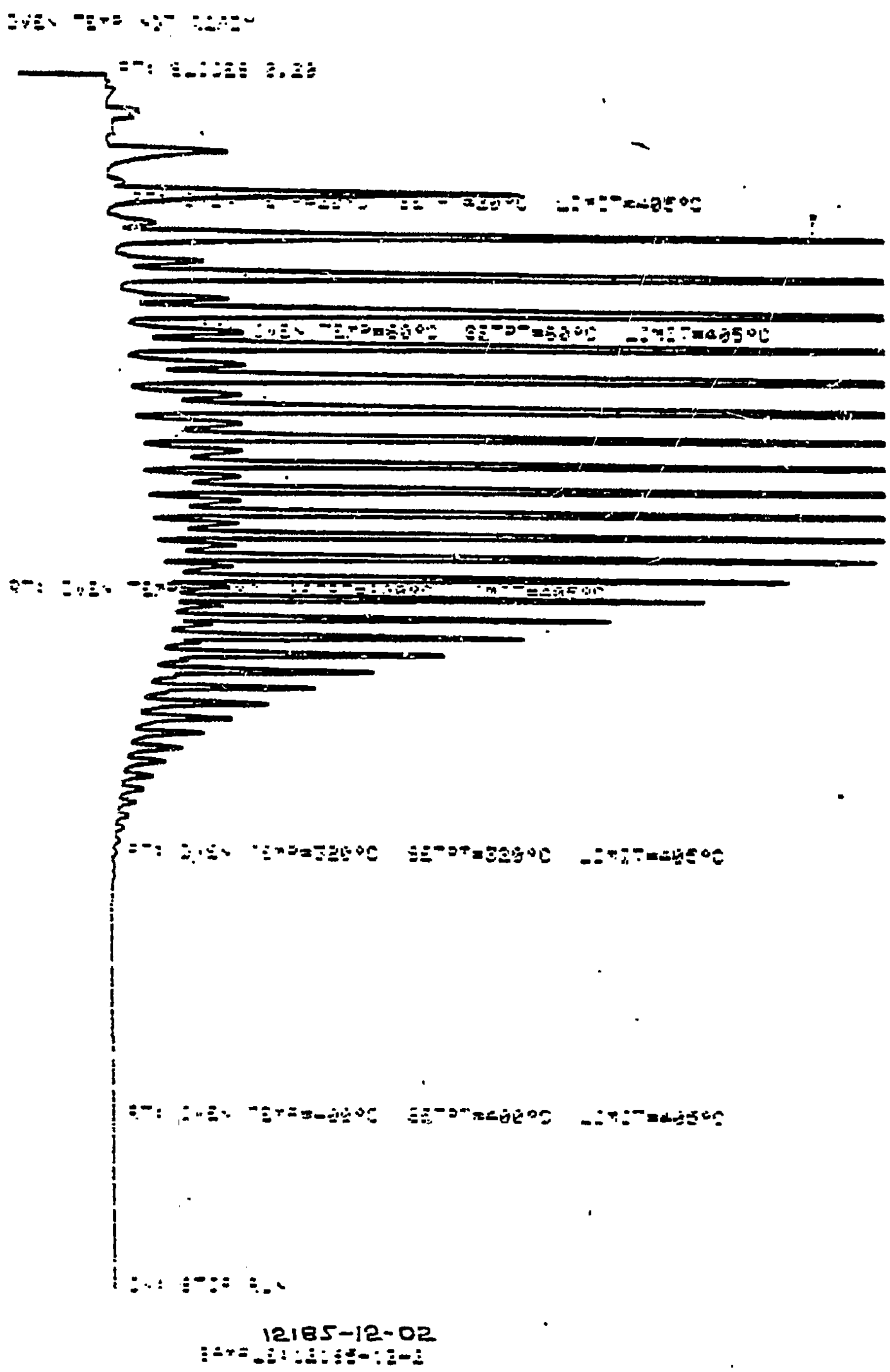


Fig. B296

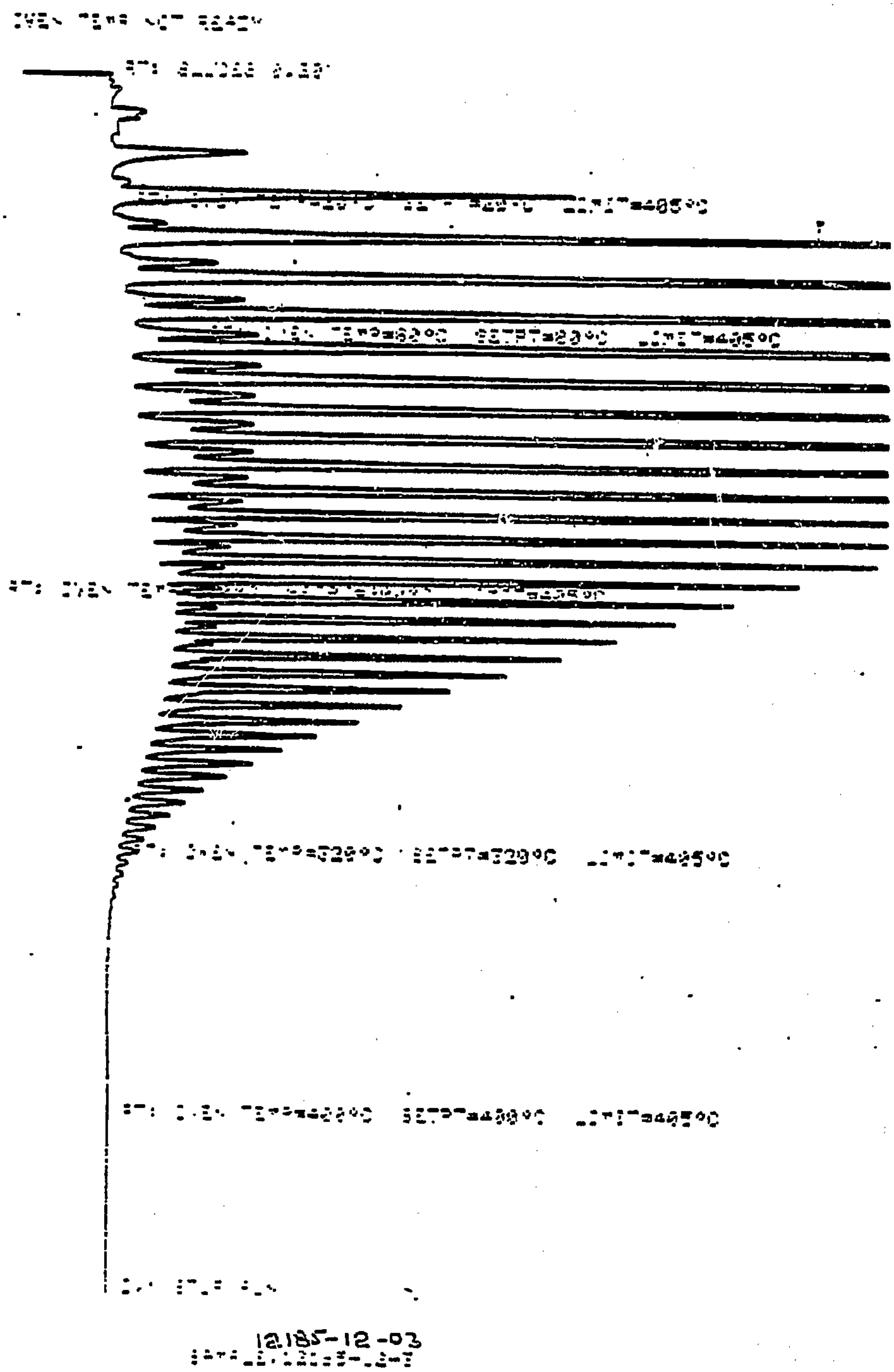
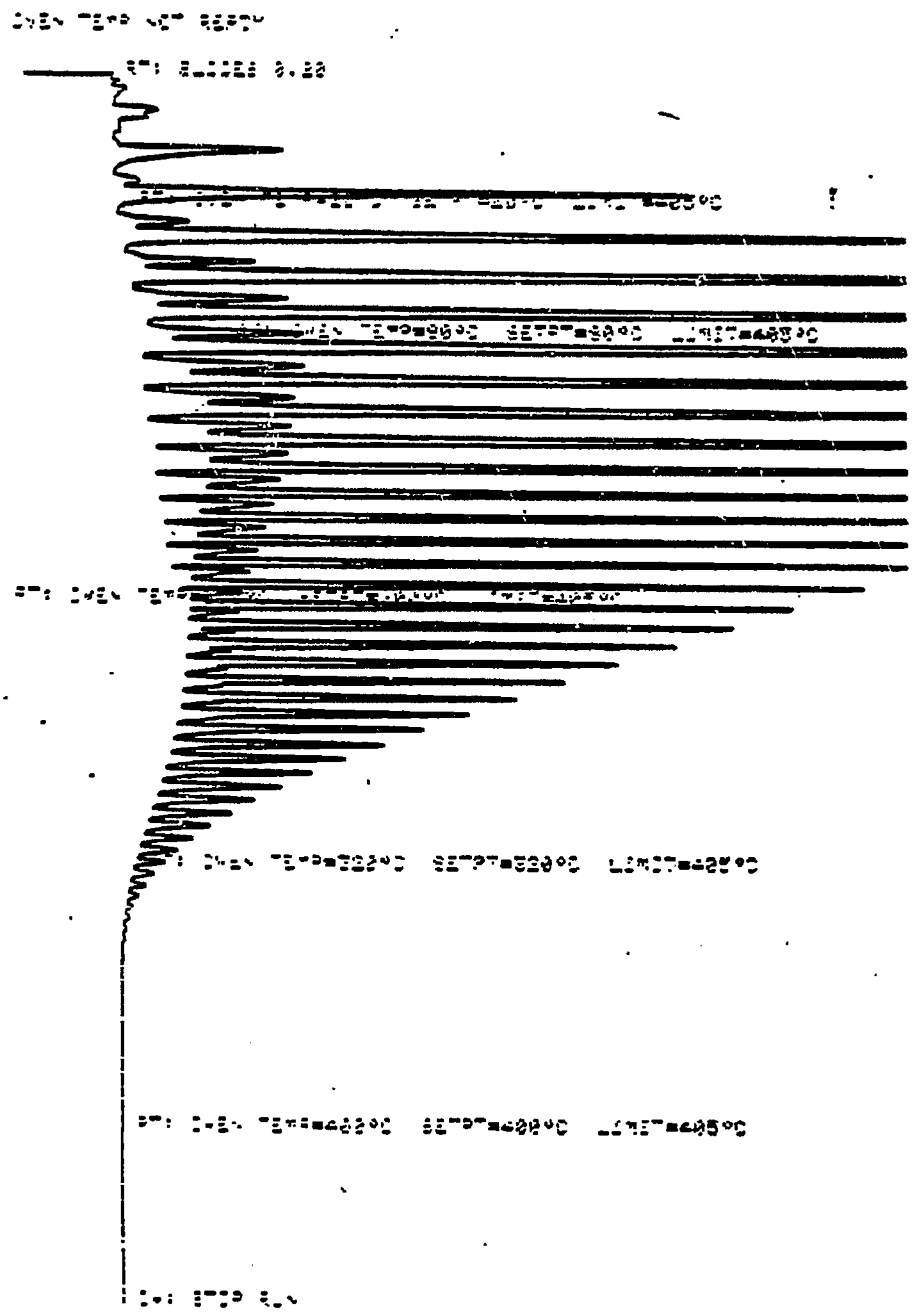


Fig. B297



12185-12-04

Fig. B298

RESULT OF SYNGAS OPERATION

RUN NO. 12185-12
CATALYST CO/X9/X10/X4-U103 12251-33-13 250 CC 106.5 G (WT GAIN +44 G)
FEED H2:CO OF 50:50 @1260 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-12-01	185-12-02	185-12-03	185-12-04
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	21.5	45.5	69.5	93.5
PRESSURE,PSIG	300	300	300	300
TEMP. C	263	259	258	260
FEED CC/MIN	1260	1260	1260	1260
HOURS FEEDING	21.50	24.00	24.00	24.00
EFFLNT GAS LITER	571.25	805.85	877.20	876.35
GM AQUEOUS LAYER	202.23	217.90	202.09	201.03
GM OIL	84.46	103.10	112.74	109.11
MATERIAL BALANCE				
GM ATOM CARBON %	82.63	91.37	95.59	97.16
GM ATOM HYDROGEN %	89.21	97.92	102.28	101.52
GM ATOM OXYGEN %	92.20	97.12	97.23	98.55
RATIO CHX/(H2O+CO2)	0.7819	0.8564	0.9560	0.9632
RATIO X IN CHX	2.3768	2.3612	2.3601	2.3768
USAGE H2/CO PRODT	1.7463	1.8556	1.7999	1.7725
FEED H2/CO FEB EFFLNT	1.0797	1.0717	1.0701	1.0448
RESIDUAL H2/CO RATIO	0.3438	0.4568	0.5194	0.4855
RATIO CO2/(H2O+CO2)	0.2053	0.1478	0.1455	0.1578
K SHIFT IN EFFLNT	0.0888	0.0792	0.0885	0.0910
SPECIFIC ACTIVITY SA	4.0824	2.5030	2.1217	2.1427
CONVERSION				
ON CO %	52.47	43.96	43.01	43.46
ON H2 %	84.87	76.11	72.33	73.73
ON CO+H2 %	69.29	60.59	58.17	58.93
PRDT SELECTIVITY,WT %				
CH4	13.29	12.37	12.19	13.01
C2 HC'S	2.04	1.94	1.79	1.95
C3H8	2.41	2.39	2.45	2.60
C3H6=	2.52	2.33	2.12	2.20
C4H10	2.38	2.38	2.38	2.52
C4H8=	3.51	3.03	2.79	2.96
C5H12	3.03	2.97	2.94	3.25
C5H10=	3.38	2.79	2.65	2.78
C6H14	4.47	3.54	3.20	3.41
C6H12= & CYCLO'S	2.10	1.81	1.59	1.61
C7+ IN GAS	9.81	8.44	7.06	7.78
LIQ HC'S	51.05	56.02	58.83	55.91
TOTAL	100.00	100.00	100.00	100.00

Table B22

SUB-GROUPING				
C1 -C4	26.16	24.43	23.73	25.24
C5 -420 F	45.25	40.83	38.62	39.53
420-700 F	25.22	28.29	27.30	24.83
700-END PT	3.37	6.44	10.35	10.40
C5+-END PT	73.84	75.57	76.27	74.76
ISO/NORMAL MOLE RATIO				
C4	0.0170	0.0175	0.0177	0.0184
C5	0.0511	0.0496	0.0522	0.0568
C6	0.3592	0.0636	0.0361	0.0368
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	0.9136	0.9794	1.1050	1.1290
C4	0.6563	0.7586	0.8223	0.8222
C5	0.8706	1.0372	1.0799	1.1359
SCHULZ-FLORY DISTRBTN				
ALPHA (EXP(SLOPE))	0.8133	0.8418	0.8563	0.8507
RATIO CH4/(1-A)**2	3.8132	4.9409	5.8991	5.8415
ALPHA FRM CORRELATION	0.8626	0.8490	0.8428	0.8460
ALPHA (EXPTL/CORR)	0.9428	0.9915	1.0160	1.0056
W%CH4 FRM CORRELATION	11.0514	14.4390	16.1538	15.5899
W%CH4 (EXPTL/CORR)	1.2029	0.8565	0.7544	0.8348
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLR OIL	OIL WAX	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.7541	0.7484*	0.7506*	0.7400*
N, REFRACTIVE INDEX	1.4244	1.4205*	1.4228*	1.4226*
SIMULT'D DISTILATN				
10 WT % @ DEG F	257	292	294	290
16	299	306	325	308
50	453	483	494	487
84	627	667	711	724
90	669	710	766	781
RANGE(16-84 %)	328	361	386	416
WT % @ 420 F	44.00	38.00	36.00	37.00
WT % @ 700 F	93.40	88.50	82.40	81.40

Table B22, cont

XIV. Run 23 (12200-13) with Catalyst 23 ($Co/X_9/X_{10}/X_4$/UCC-103)

The purpose of this run was to test the effectiveness of X_4 obtained from a different source than that used in Runs 16 and 19.

The UCC-103 was combined with X_4 before forming in close contact, by the method used in Run 11, with cobalt oxide which had been promoted with X_9 and X_{10}. The resulting powder, after bonding with 15 percent silica, was extruded to 1/8-inch pellets. The final catalyst contained 11.5 percent cobalt, 0.50 percent X_9, 0.66 percent X_{10} and 2.21 percent X_4.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B299-302. Simulated distillations of the C_5^+ product are plotted in Figs. B302-304. Carbon number product distributions are plotted in Figs. B305-306. Chromatograms from simulated distillations are reproduced in Figs. B307-308. Detailed material balances appear in Table B23.

The initial conversion of syngas was 51.9 percent, with a specific activity of 1.0. Although slightly higher than for Catalysts 16 and 19, this is far below the initial specific activity of about 12 for both Catalysts 11 and 20.

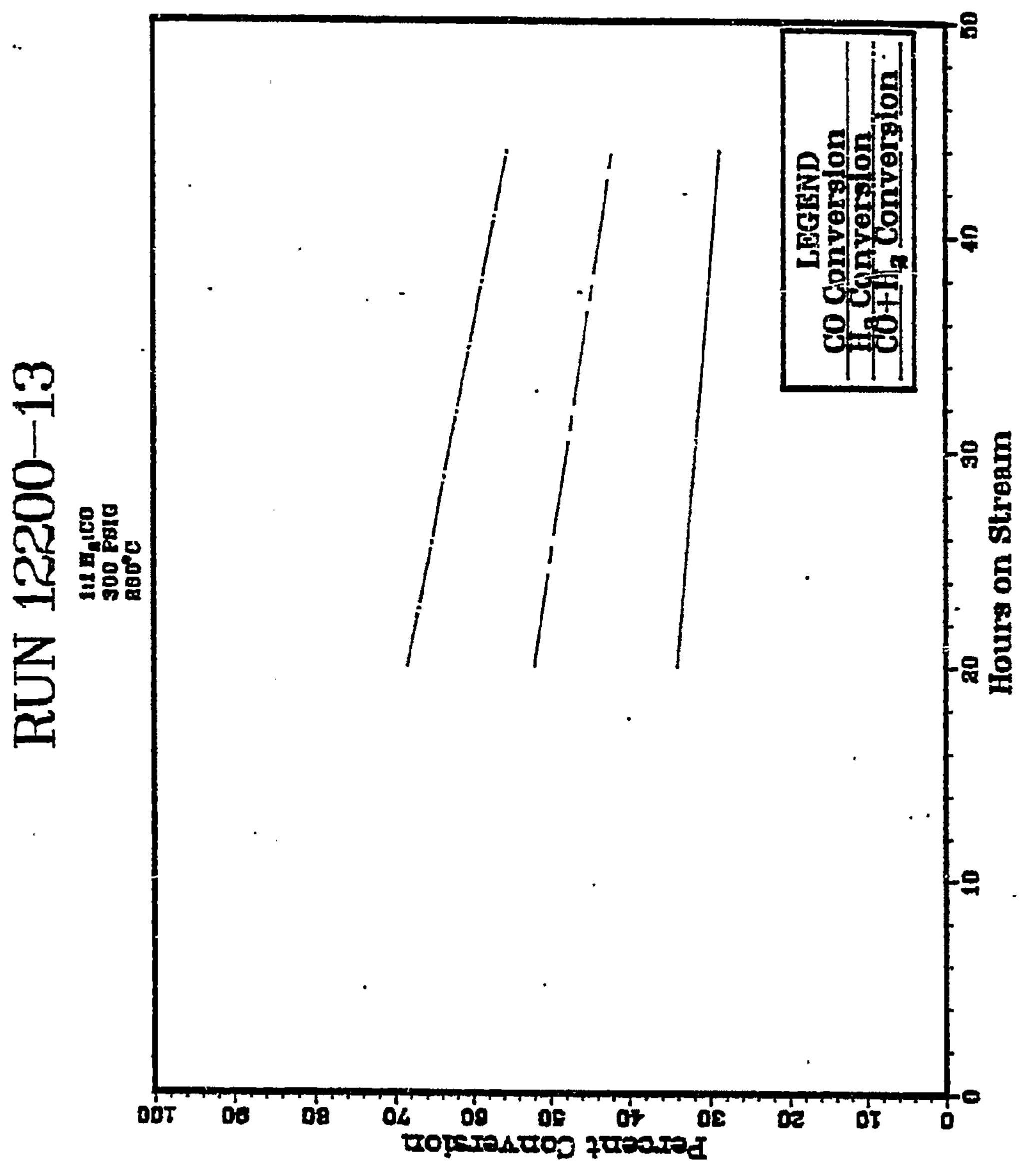

RUN 12200—13
300 PSIG
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion

Fig. B299

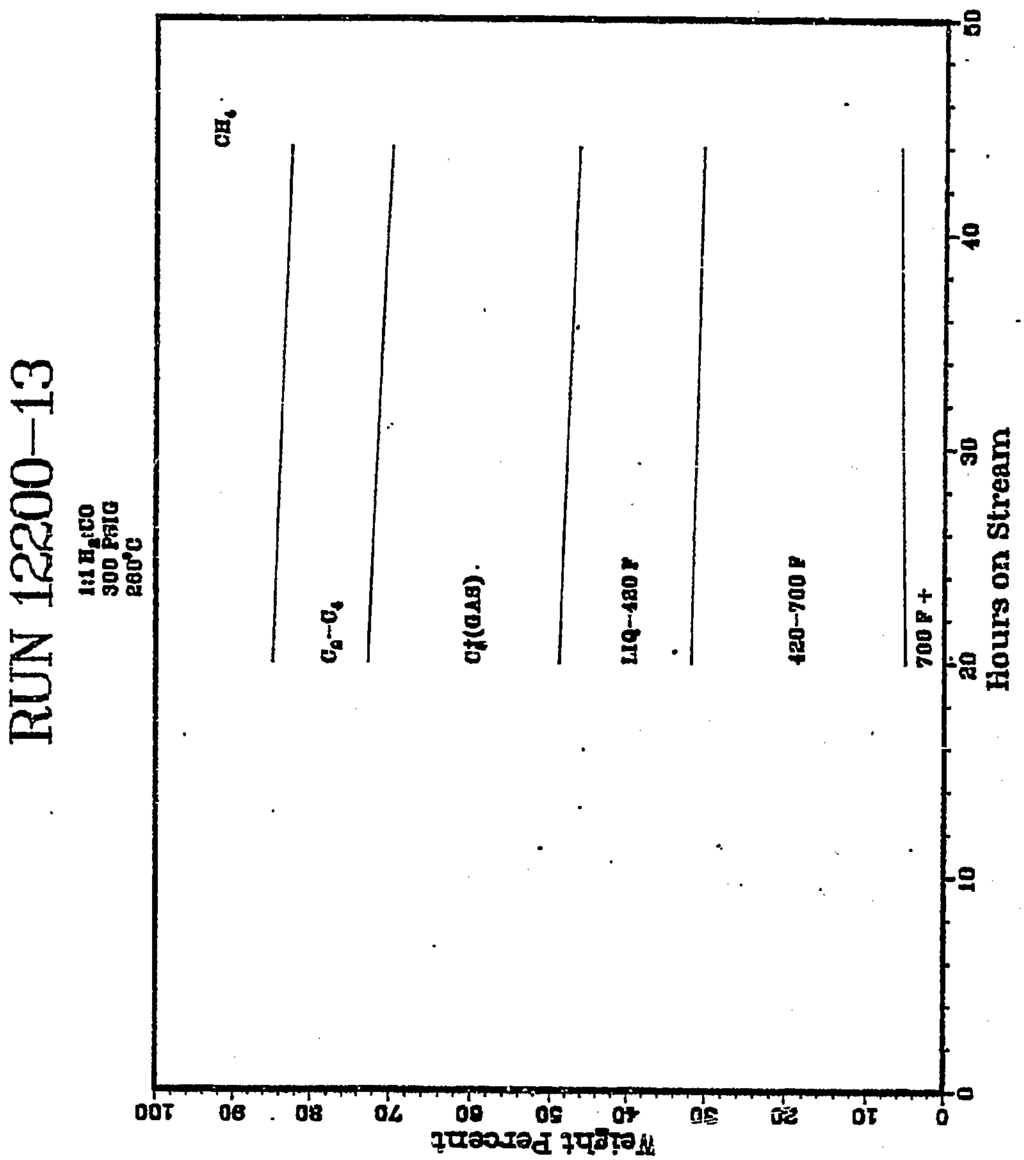

RUN 12200—13
1:1 H2:CO
300 PSIG
260°C
CH4
C2-C4
C5+(GAS)
LIQ-420 F
420-700 F
700 F+
Weight Percent
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100

Fig. B300

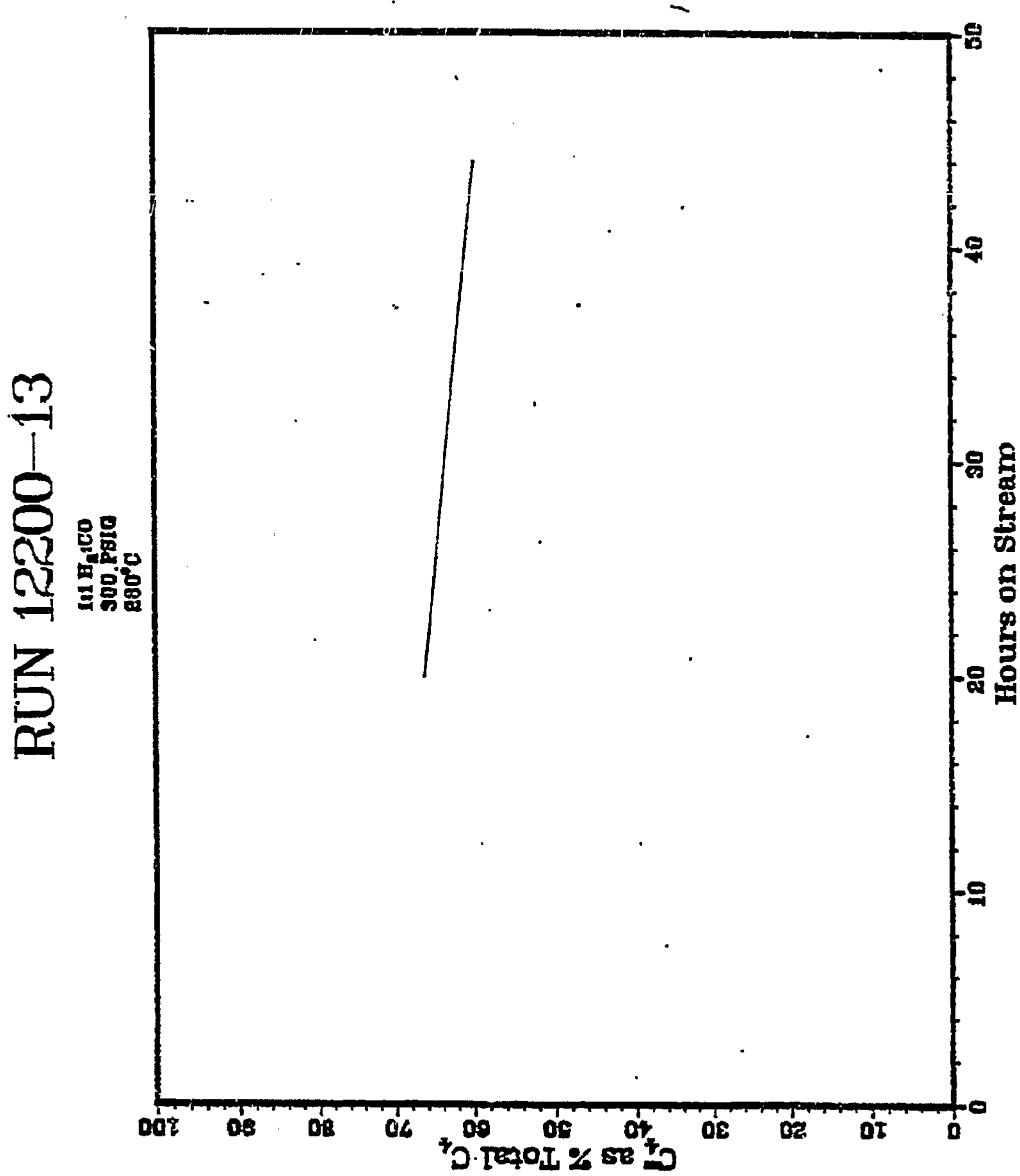


Fig. B301

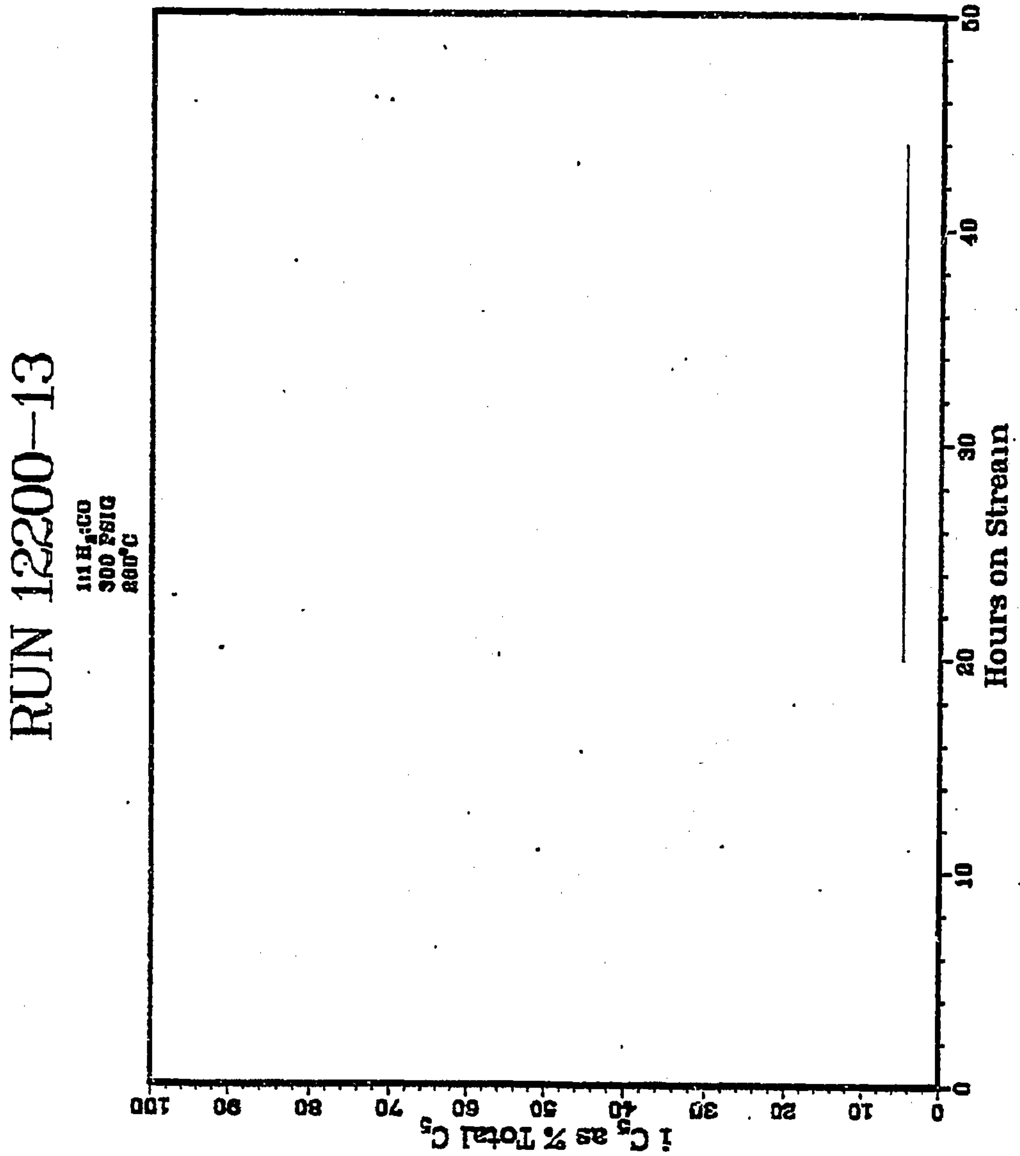
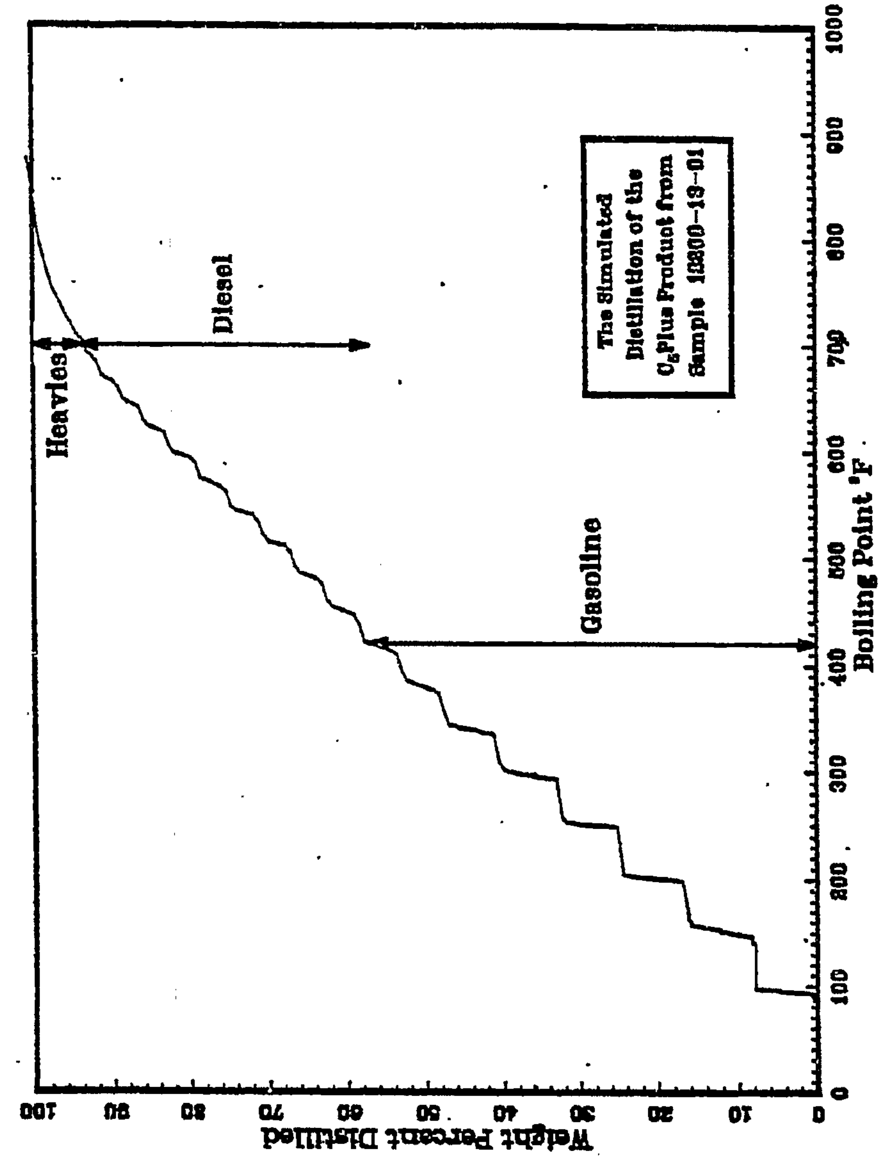


Fig. B302



Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
The Simulated

Fig. B303

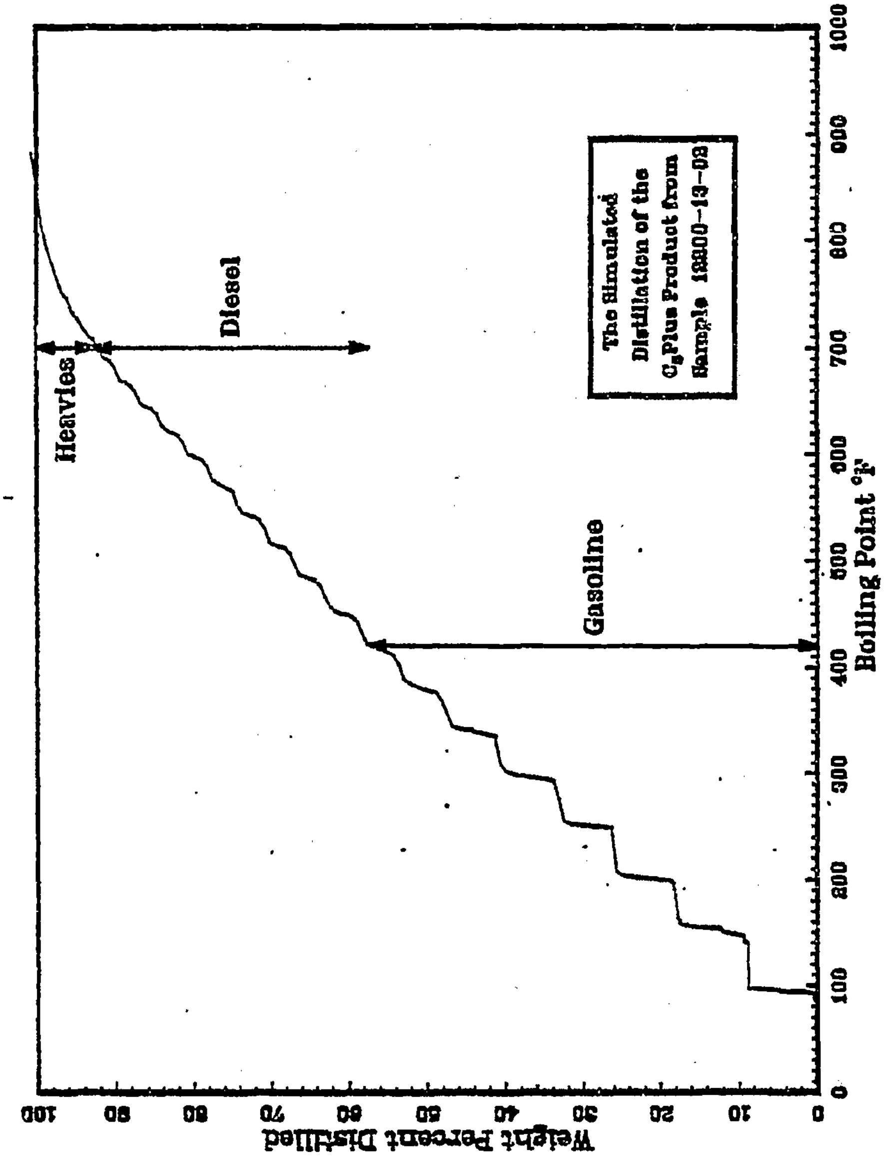
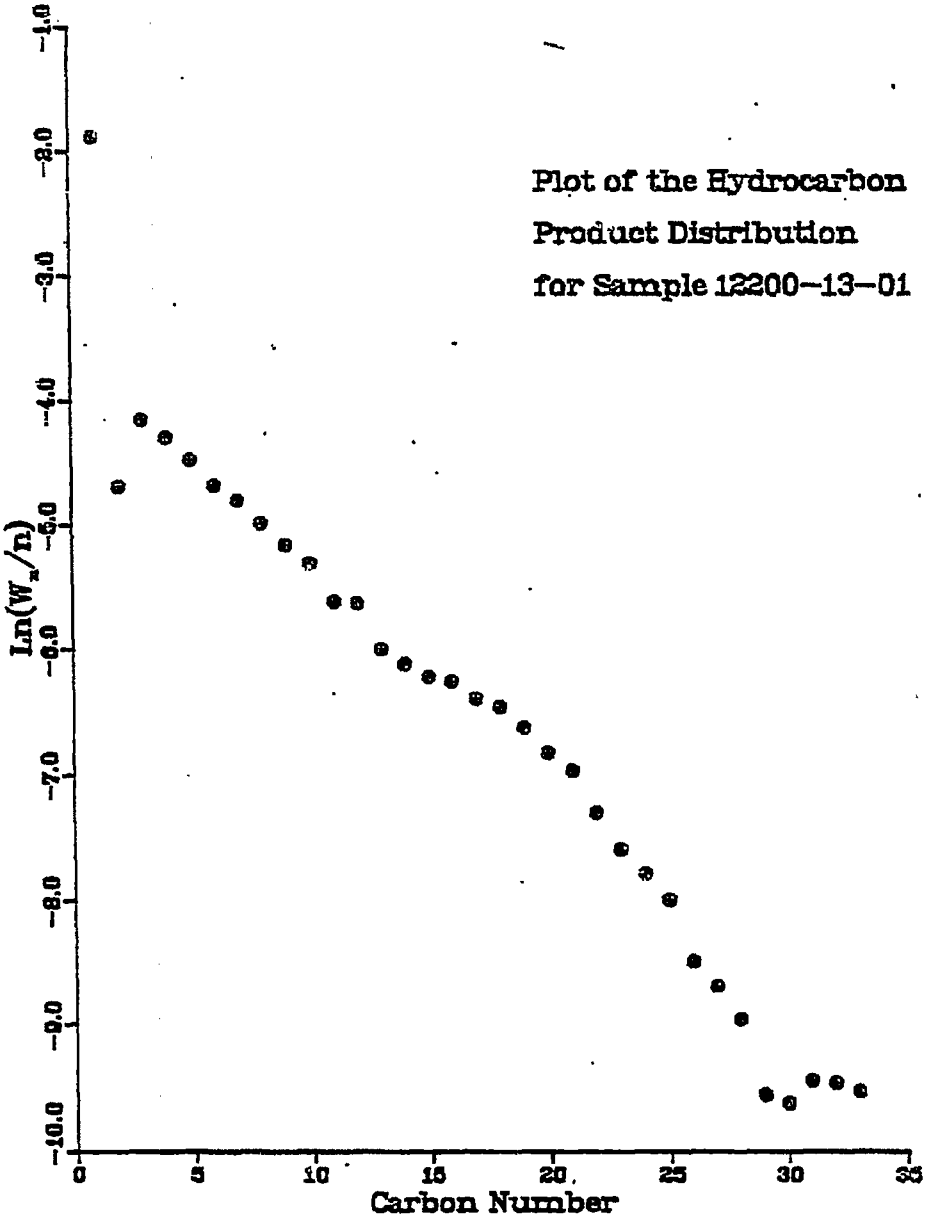
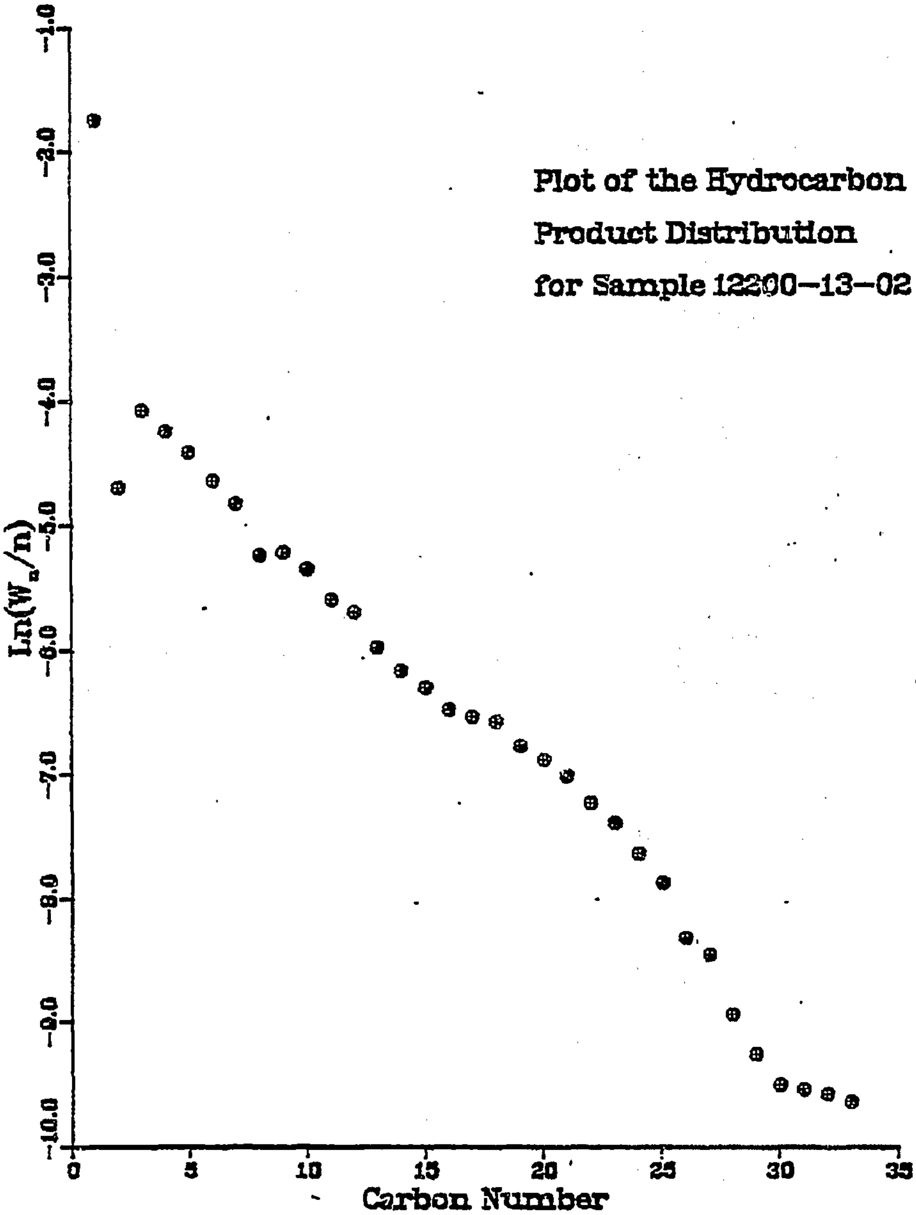

Weight Percent Distilled
Boiling Point °F
Heavies
Diesel
Gasoline
The Simulated
Distillation of the

Fig. B304



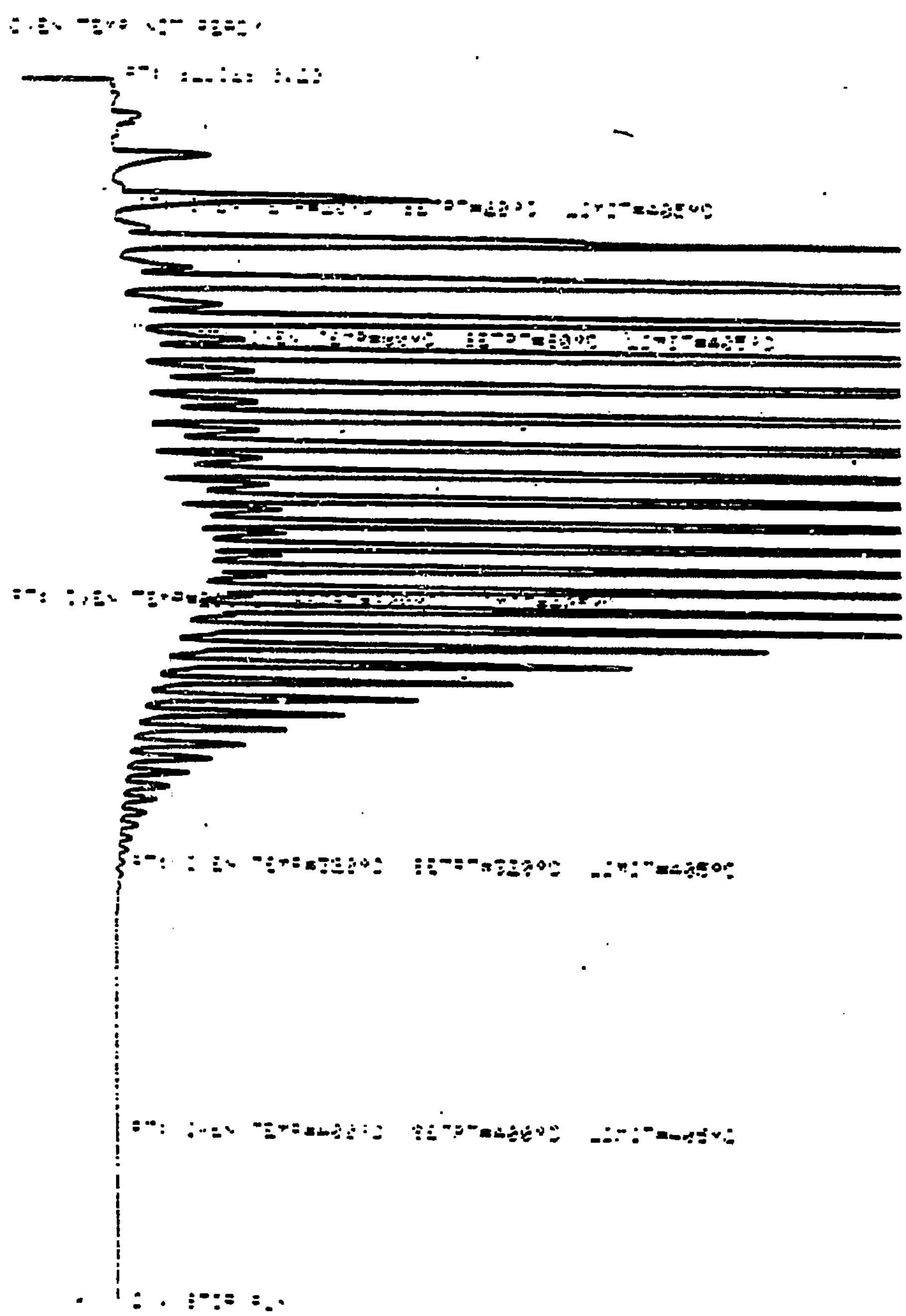
Plot of the Hydrocarbon
Product Distribution
for Sample 12200-13-01
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B305



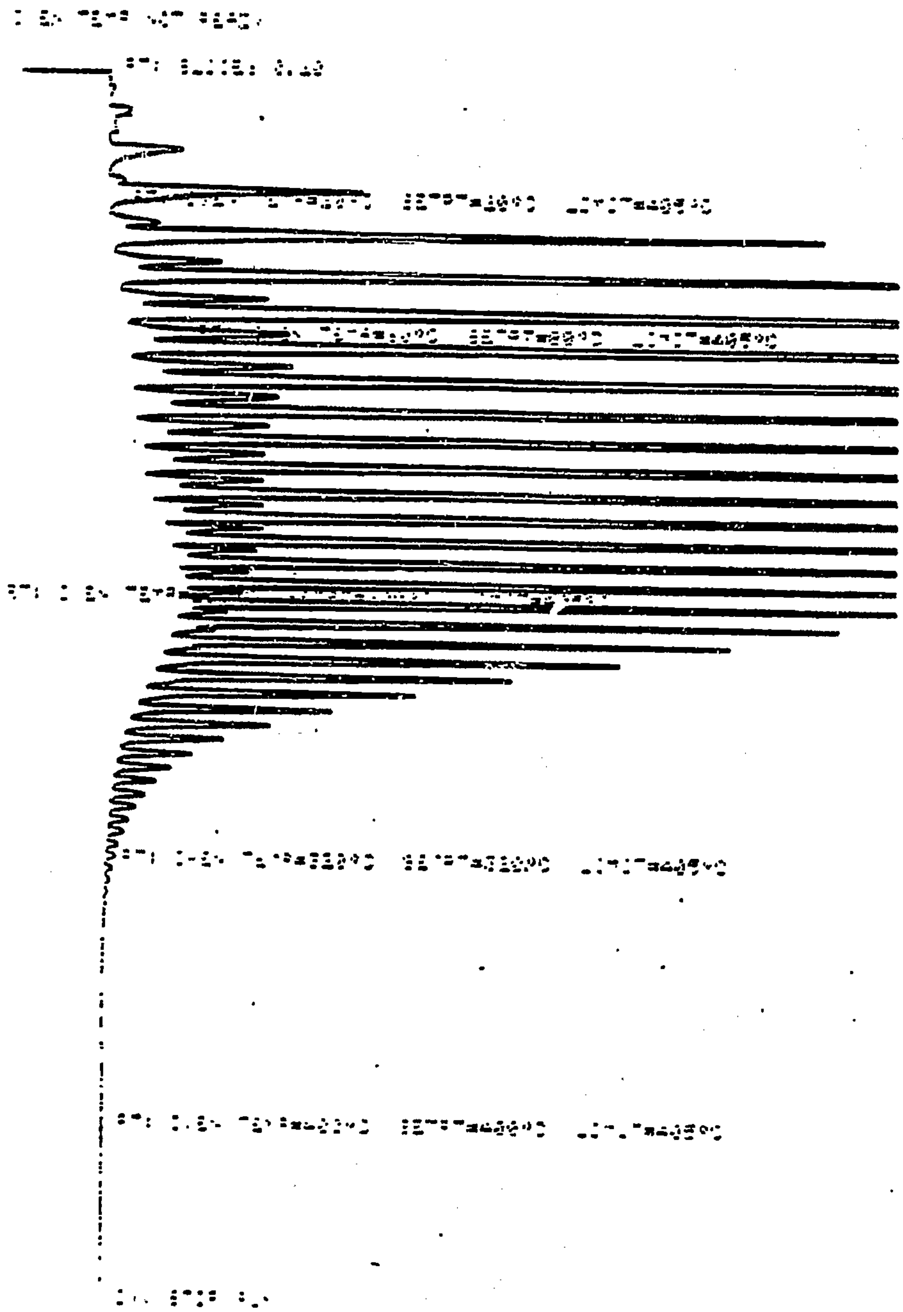
Plot of the Hydrocarbon
Product Distribution
for Sample 12200-13-02
Ln(Wn/n)
Carbon Number

Fig. B306



12200-13-01

Fig. B307



12200-13-02

Fig. B308

RESULT OF SYNGAS OPERATION

RUN NO. 12200-13
CATALYST CO/X9/X10/X4-U103 12251-36-17 250 CC 112.1G (WT CHANGE +43.5 G
FEED H2:CO OF 50:50 @1260 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-13-01	200-13-02
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	20.0	44.0
PRESSURE,PSIG	300	300
TEMP. C	263	260
FEED CC/MIN	1260	1260
HOURS FEEDING	20.00	24.00
EFFLNT GAS LITER	691.95	1133.80
GM AQUEOUS LAYER	173.42	142.57
GM OIL	49.13	61.09
MATERIAL BALANCE		
GM ATOM CARBON %	79.50	97.73
GM ATOM HYDROGEN %	86.96	96.31
GM ATOM OXYGEN %	94.47	100.61
RATIO CHX/(H2O+CO2)	0.5992	0.8940
RATIO X IN CHX	2.3916	2.4409
USAGE H2/CO PRODT	2.1973	1.9024
FEED H2/CO FRM EFFLNT	1.0940	0.9855
RESIDUAL H2/CO RATIO	0.5247	0.6171
RATIO CO2/(H2O+CO2)	0.1251	0.1345
K SHIFT IN EFFLNT	0.0750	0.0959
SPECIFIC ACTIVITY SA	1.0958	0.8439
CONVERSION		
ON CO %	34.03	28.66
ON H2 %	68.36	55.33
ON CO+H2 %	51.97	41.90
PRDT SELECTIVITY,WT %		
CH4	15.23	17.44
C2 HC'S	1.84	1.83
C3H8	1.75	2.34
C3H6=	3.00	2.77
C4H10	1.89	2.37
C4H8=	3.58	3.40
C5H12	2.37	2.94
C5H10=	3.35	3.16
C6H14	2.95	3.54
C6H12= & CYCLO'S	2.61	2.24
C7+ IN GAS	12.51	11.54
LIQ HC'S	48.92	46.44
TOTAL	100.00	100.00

Table B23

SUB-GROUPING		
C1 -C4	27.29	30.14
C5 -420 F	40.91	39.44
420-700 F	26.66	24.52
700-END PT	5.14	5.90
C5+-END PT	72.71	69.86
ISO/NORMAL MOLE RATIO		
C4	0.0175	0.0140
C5	0.0500	0.0488
C6	0.0890	0.0990
C4=	0.0000	0.0000
PARAFFIN/OLEFIN RATIO		
C3	0.5564	0.8057
C4	0.5090	0.6725
C5	0.6887	0.9055
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8358	0.8389
RATIO CH4/(1-A)**2	5.6494	6.7210
ALPHA FRM CORRELATION	0.8420	0.8343
ALPHA (EXPTL/CORR)	0.9926	1.0055
W%CH4 FRM CORRELATION	17.4411	19.2147
W%CH4 (EXPTL/CORR)	0.8733	0.9075
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.7527*	0.7530*
N, REFRACTIVE INDEX	1.4245*	1.4245*
SIMULT'D DISTILATN		
10 WT % @ DEG F	299	300
16	340	341
50	506	507
84	666	682
90	706	718
RANGE(16-84 %)	326	341
WT % @ 420 F	35.00	34.50
WT % @ 700 F	89.50	87.30

Table B23, cont

XV. Run 24 (12185-13) with Catalyst 24 ($Co/X_9/X_{10}$/UCC-113)

The purpose of this run was to test a newly developed shape-selective component, UCC-113, being used in place of UCC-103 in a formulation similar to that of Catalyst 20 (Run 12185-11).

Formulation of the catalyst was similar in method to that of Catalyst 20 except that UCC-113 was substituted for UCC-103. Cobalt oxide was promoted with X_9 and X_{10}, then formed in close contact with UCC-113 by the method used in Run 11. The resulting powder, after bonding with 15 percent silica, was extruded to 1/8-inch pellets. The final catalyst contained 7.9 percent cobalt, 0.37 percent X_9 and 0.50 percent X_{10}.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B309-312. Simulated distillations of the C_5^+ product are plotted in Figs. B313-319. Carbon number product distributions are plotted in Figs. B320-326. Chromatograms from simulated distillations are reproduced in Figs. B327-333. Detailed material balances appear in Tables B24-25.

Between Sample 2 of the run at 42.5 hours on stream, and Sample 3 at 66.5 hours, the temperature in the reactor rose briefly from the design value of 260C to nearly 290C when the temperature controllers malfunctioned. The vertical dotted lines in Figs. B309-312 indicate the time when this occurred.

The initial conversion of syngas was 90.1 percent, with a specific activity of 11.8, characteristic of the high initial activity levels with this type of formulation. Comparable values for Catalyst 20 were 88.2 percent and 7.6, so that this catalyst was a little more active on a volume basis. Since it contained only two-thirds as much cobalt, however, on a basis of percent cobalt its activity was considerably higher.

The initial water gas shift activity was, characteristically, also very high.

Once again, however, the catalyst deactivated rather quickly during the early part of the run. From its initial value of 90.1 percent, the syngas conversion dropped to 55.7 percent at 114 hours on stream. During the last 48 hours of the run, from 114.5 to 162.5 hours on stream, the conversion appeared to hold fairly stable at a rate of about 57.8 percent and a specific activity of about 1.5.

The product distribution was similar to that of Catalyst 20, except weighted a little more toward the heavies. The Schulz-Flory plots, which show a fairly linear product distribution, lack any indication of a carbon number cutoff such as appeared for Catalyst 20. The quality of product of the two catalysts was closely similar.

Subject to allowance for the temperature-control anomaly, this run demonstrated that UCC-113, as well as UCC-103, can be used to produce a catalyst of high activity, at least initially. Further investigation appears to be indicated.

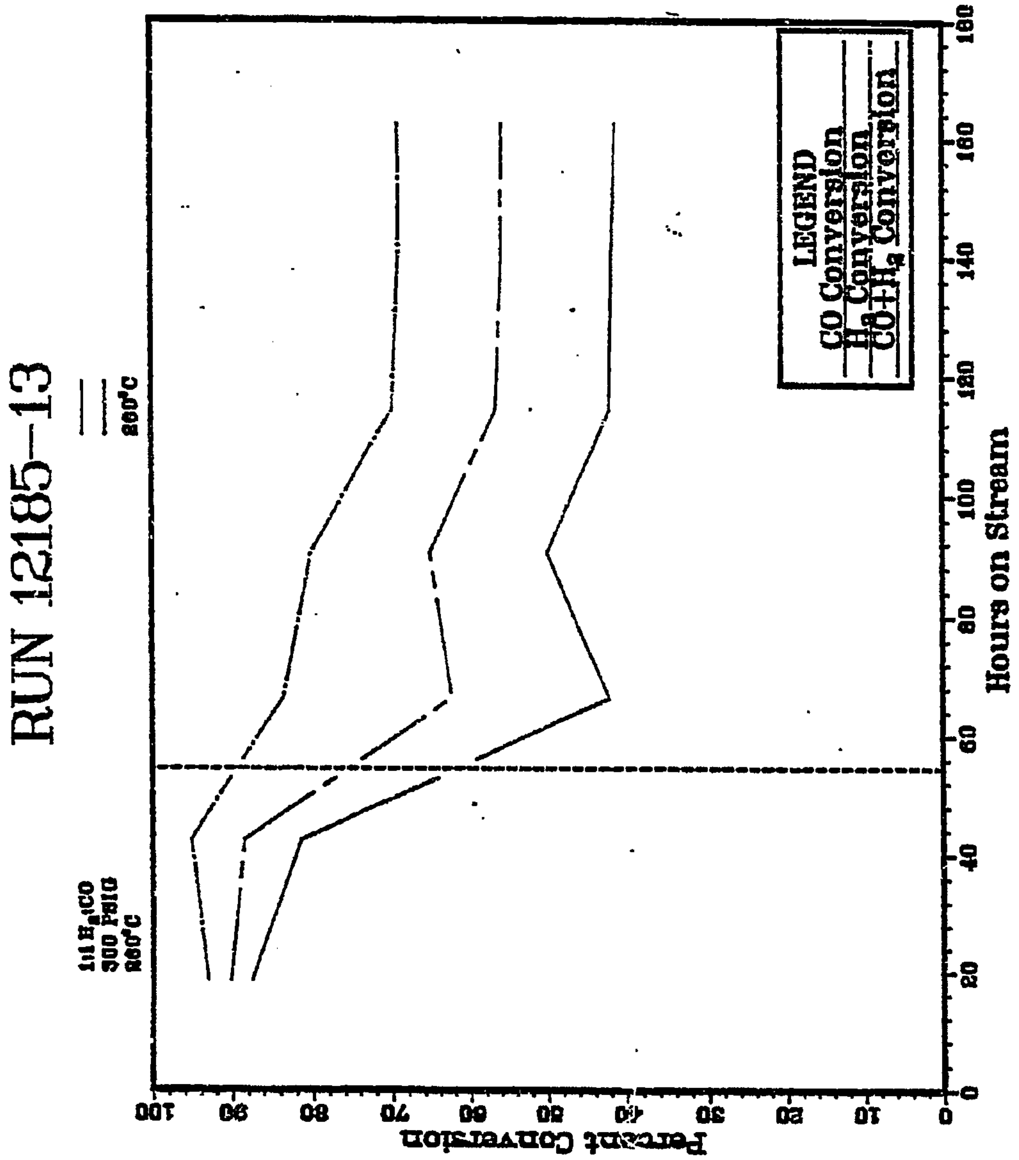

RUN 12185-13
1:1 H2:CO
300 PSIG
260°C
280°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
120
140
160
180

Fig. B309

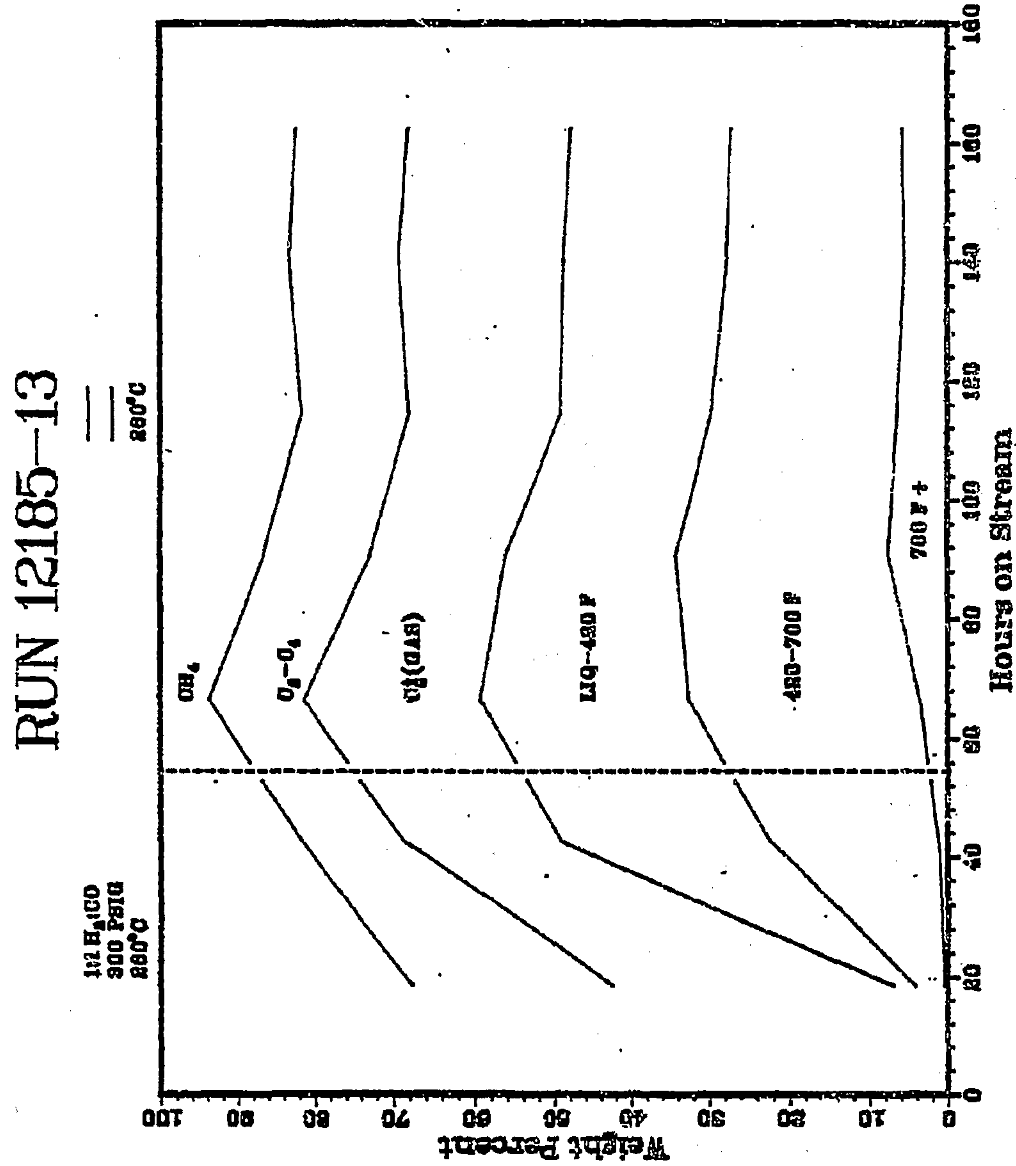

RUN 12185–13
Weight Percent
Hours on Stream
LIQ–430 F
430–700 F
700 F +

Fig. B310

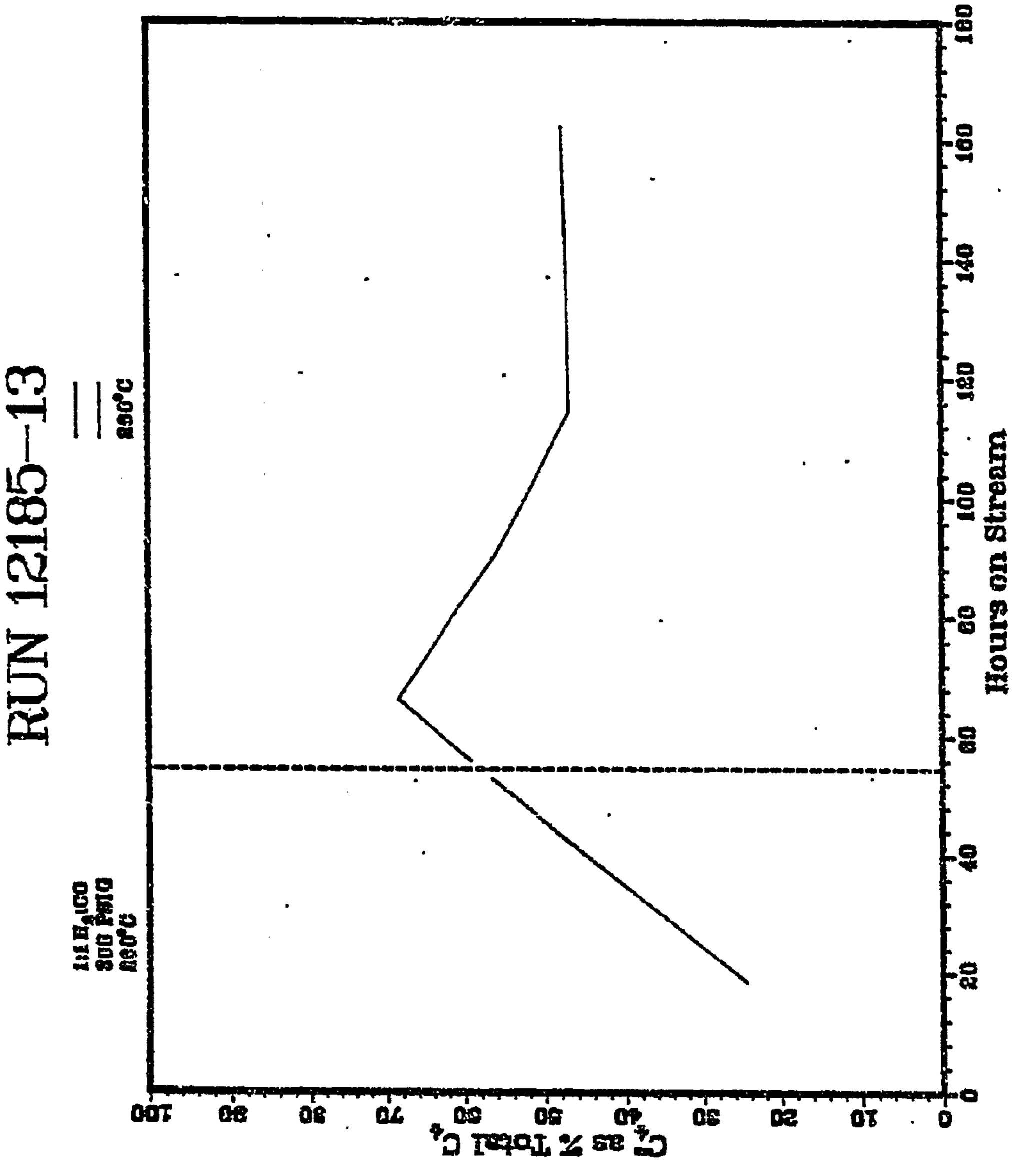


Fig. B311

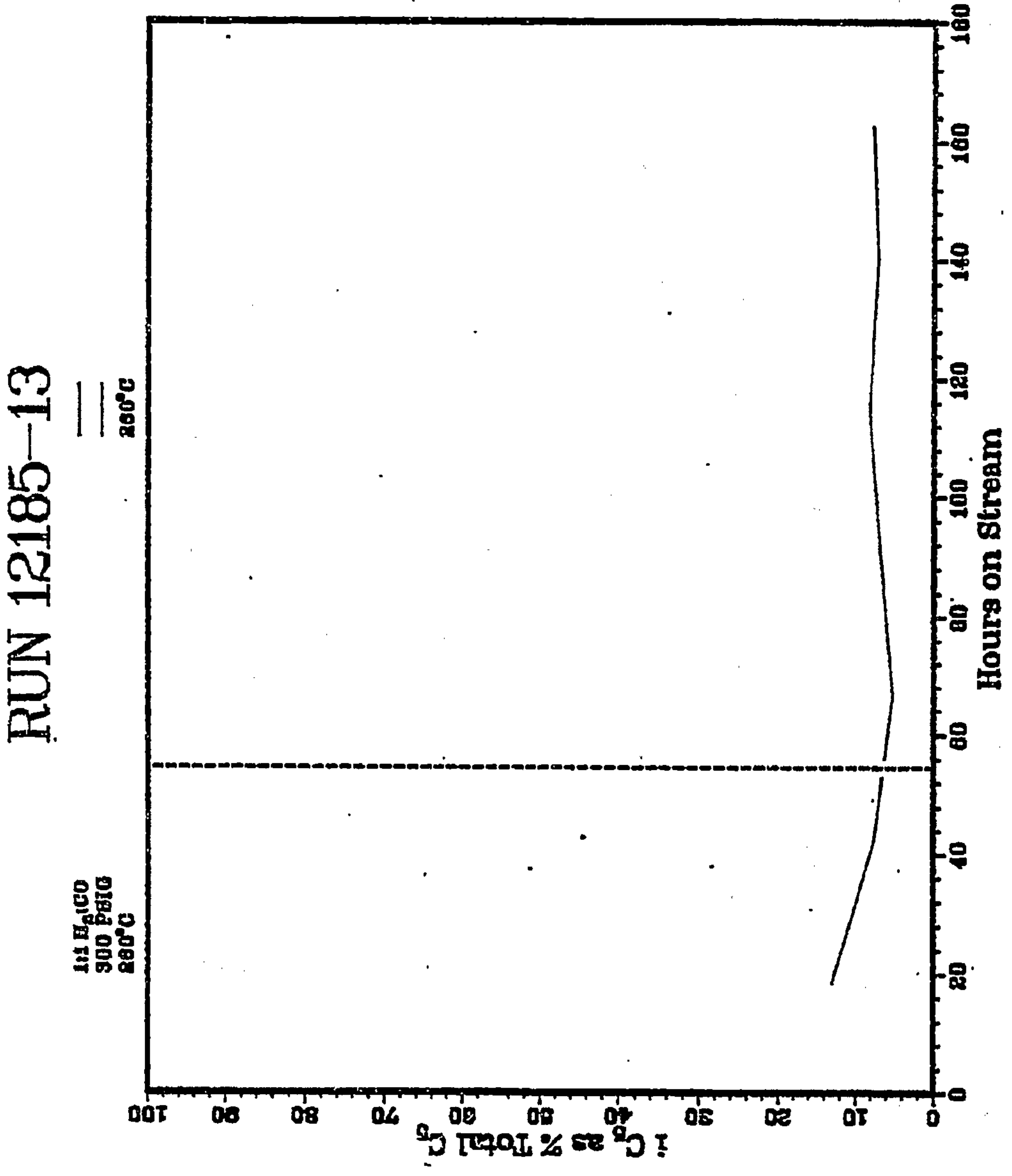

RUN 12185—13
1:1 H2:CO
300 PSIG
260°C
260°C
Hours on Stream
i C5 as % Total C5

Fig. B312

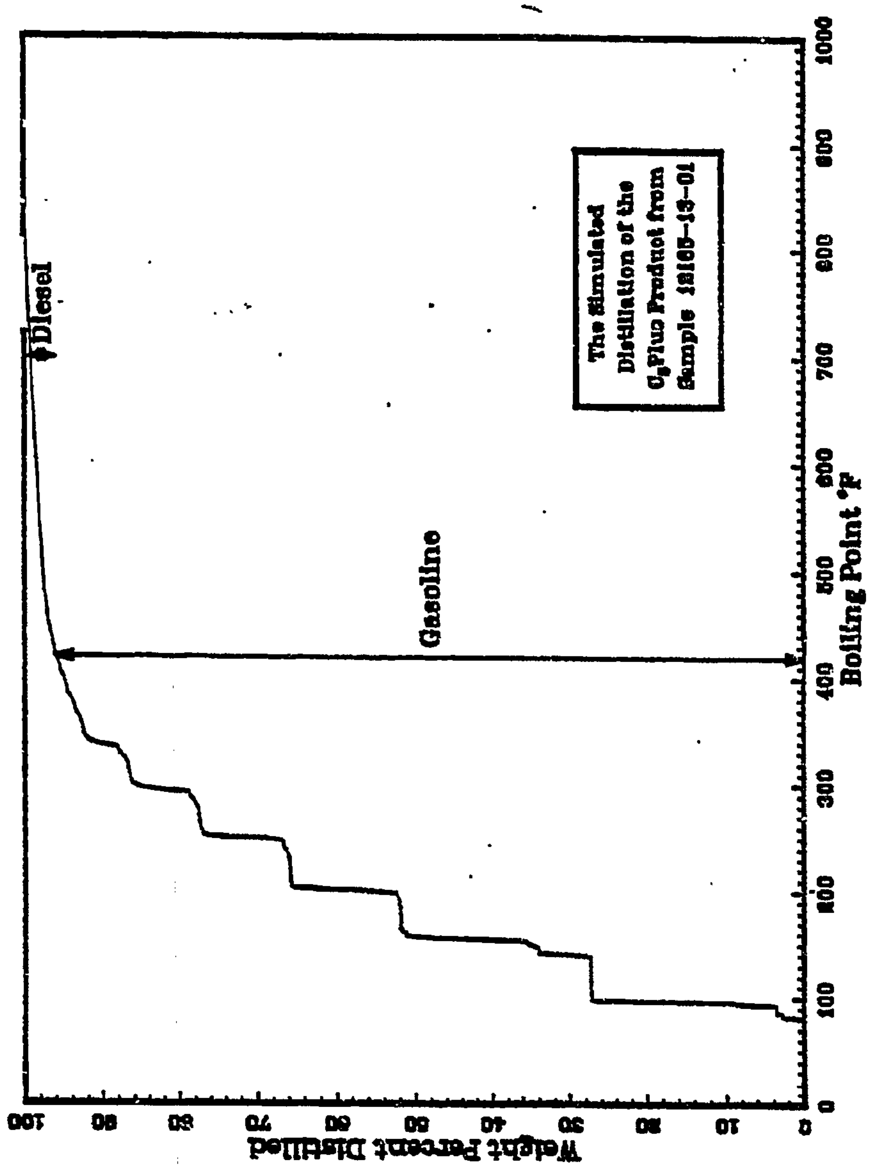
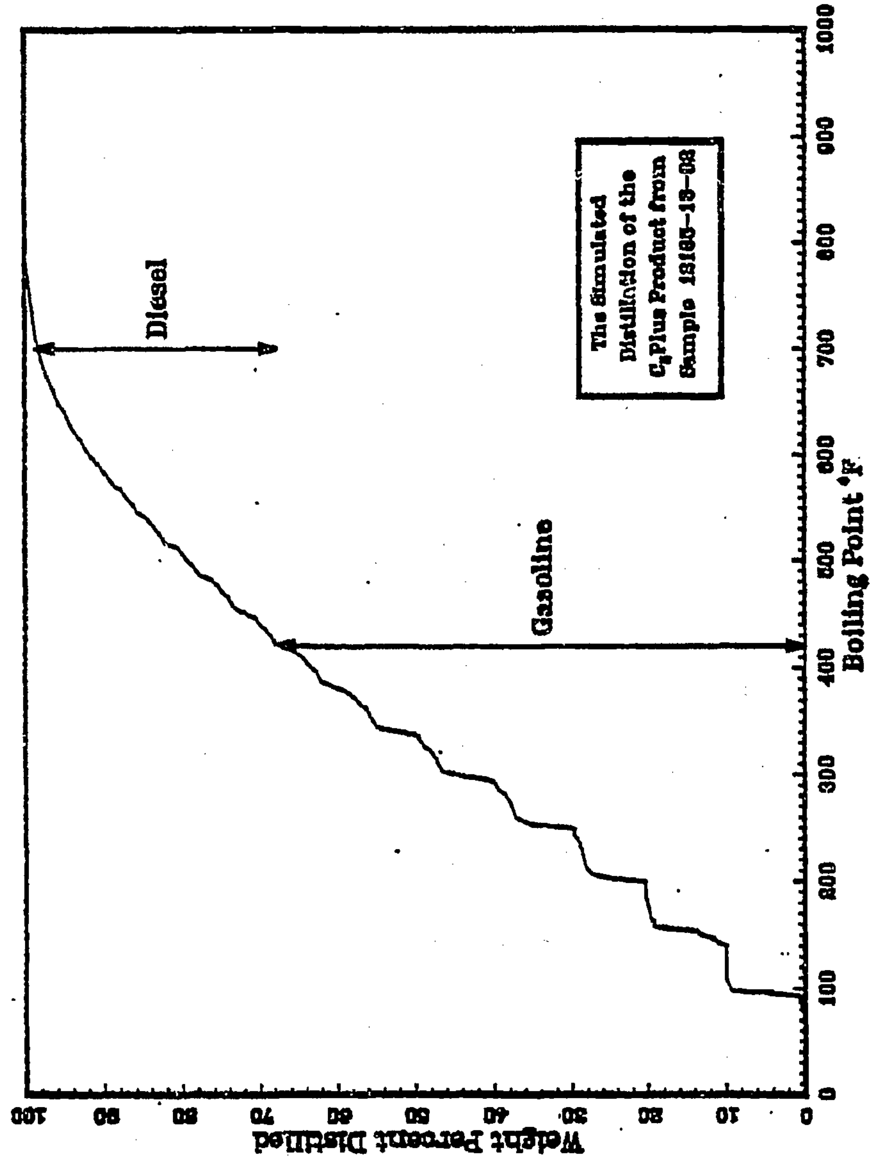

Diesel
Gasoline
The Simulated
Distillation of the
C5Plus Product from
Boiling Point °F
Weight Percent Distilled

Fig. B313



Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled
The Simulated
Distillation of the
C_5Plus Product from

Fig. B314

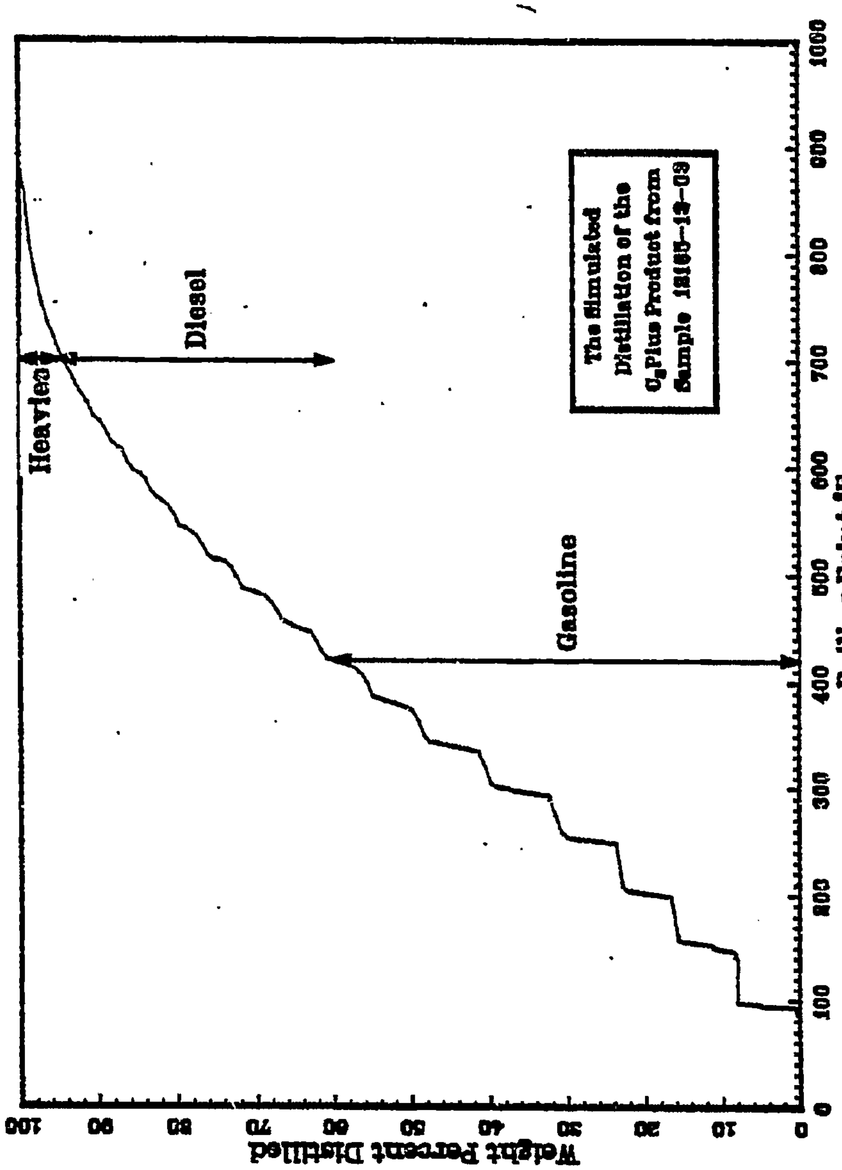
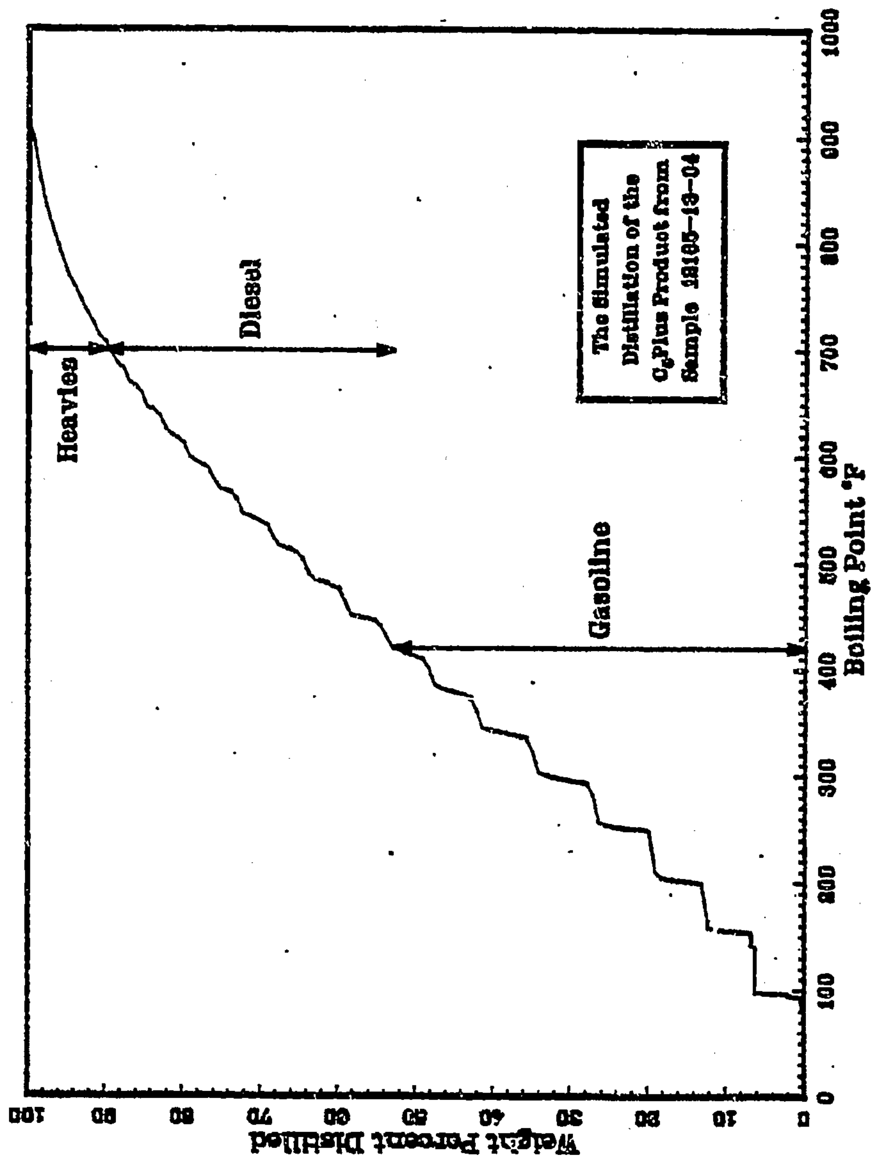

The Simulated
Distillation of the
Diesel
Heavies
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. B315



Heavies
Diesel
Gasoline
The Simulated
Distillation of the
Boiling Point °F
Weight Percent Distilled
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80
90
100

Fig. B316

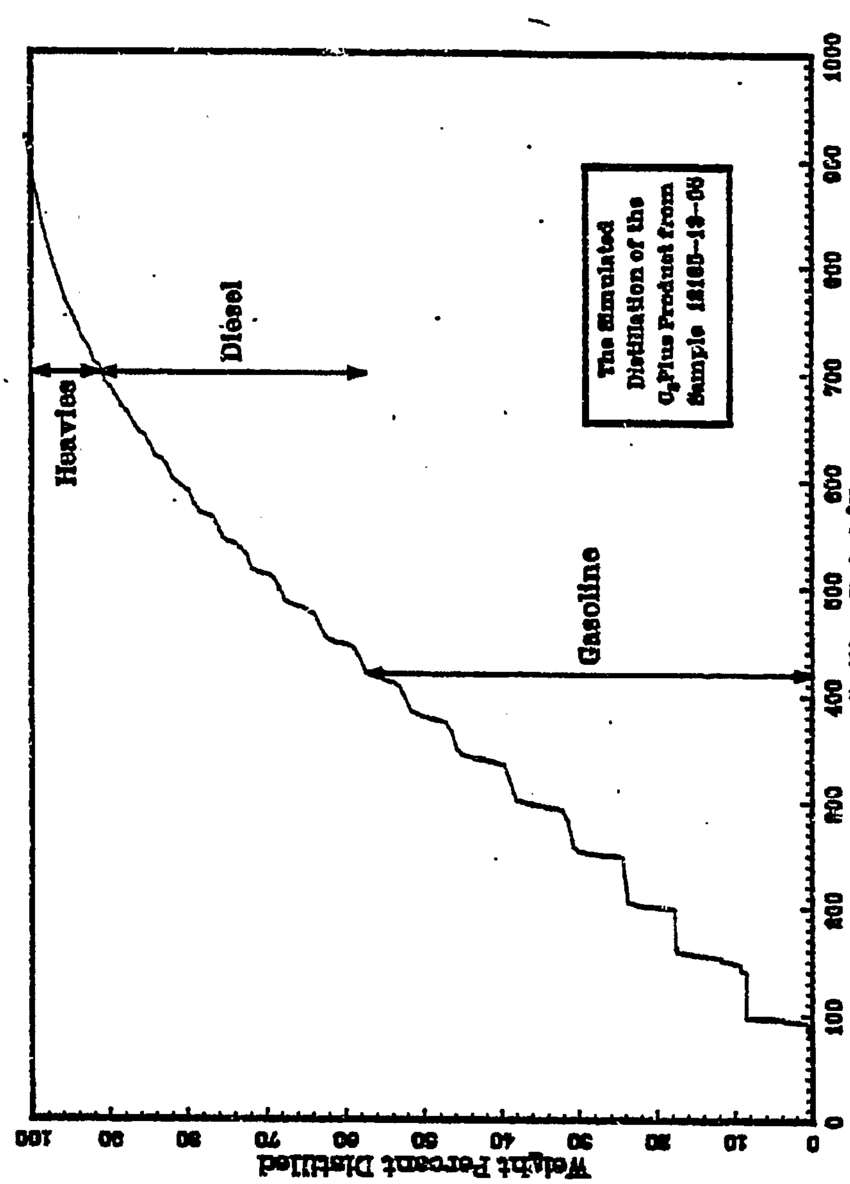

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C_5Plus Product from
Sample
Weight Percent Distilled
Boiling Point °F
0
10
20
30
40
50
60
70
80
90
100
0
100
200
300
400
500
600
700
800
900
1000

Fig. B317

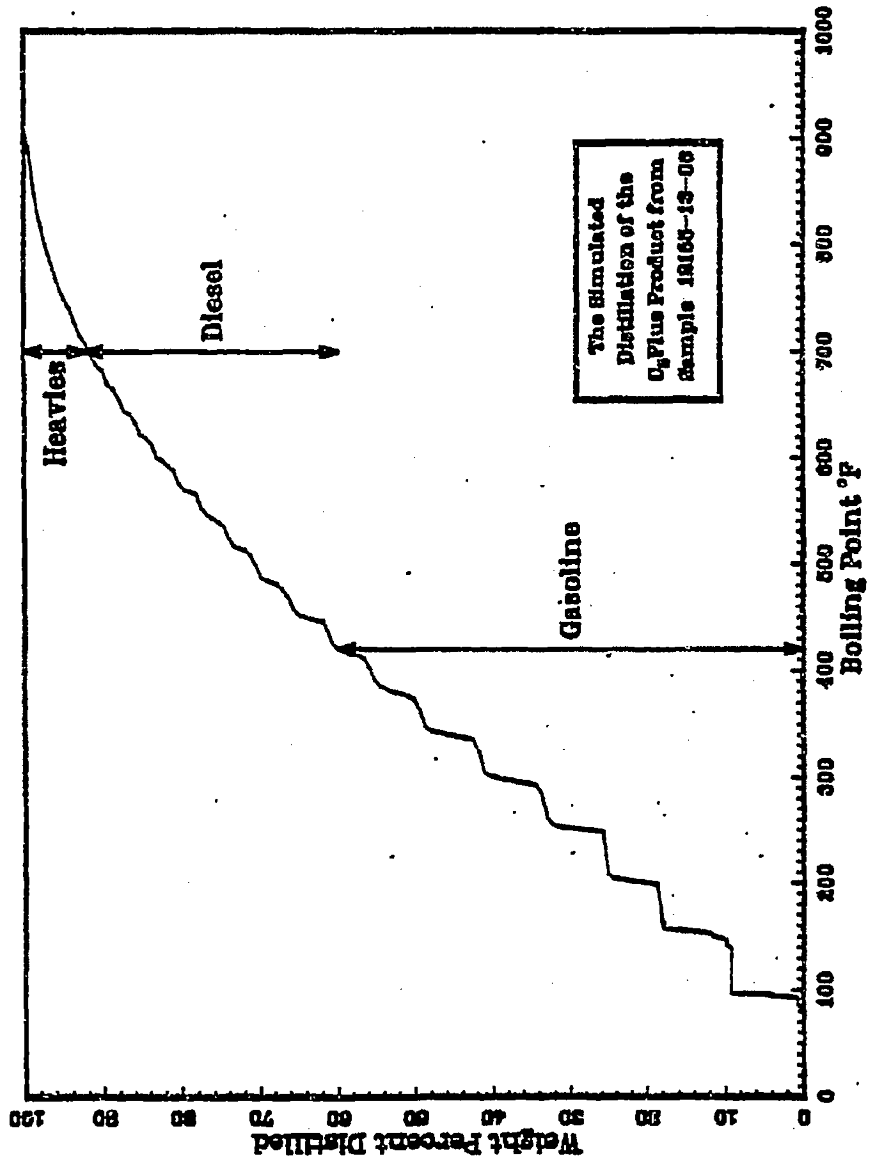
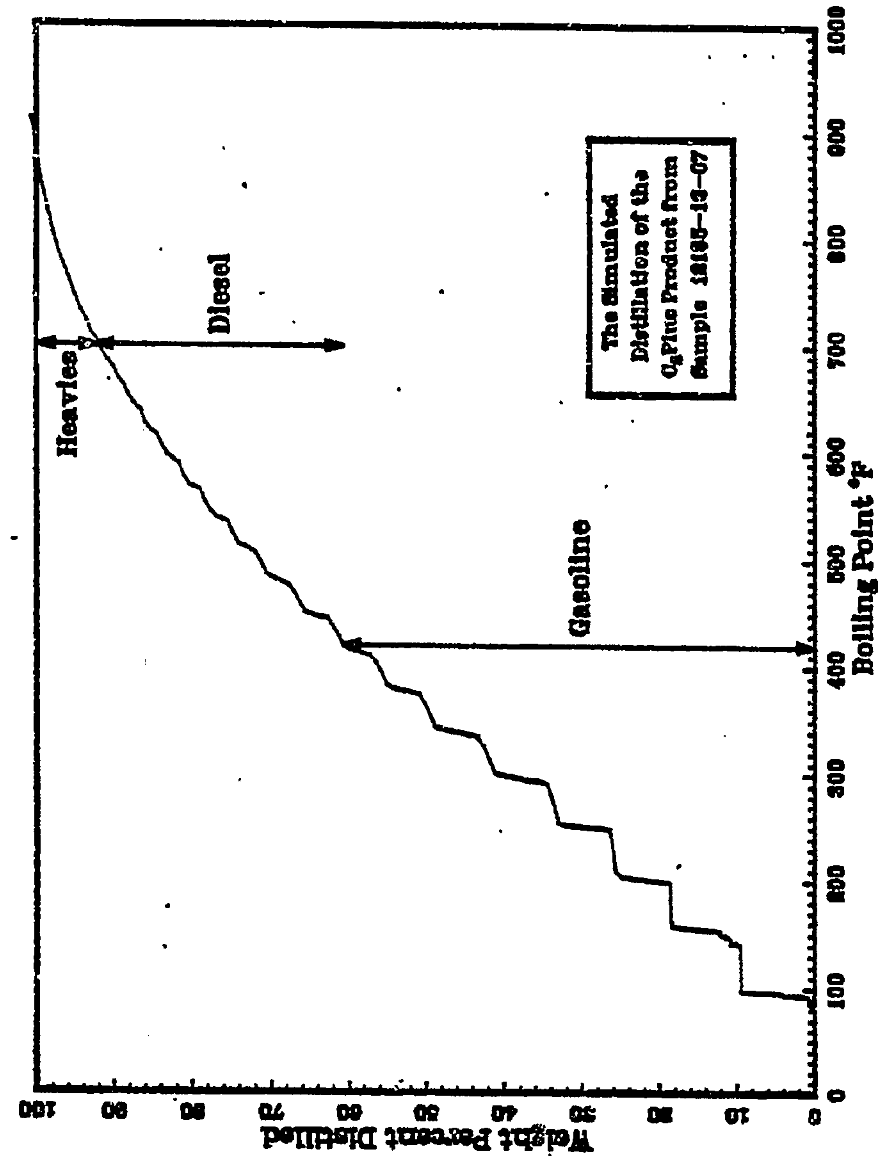
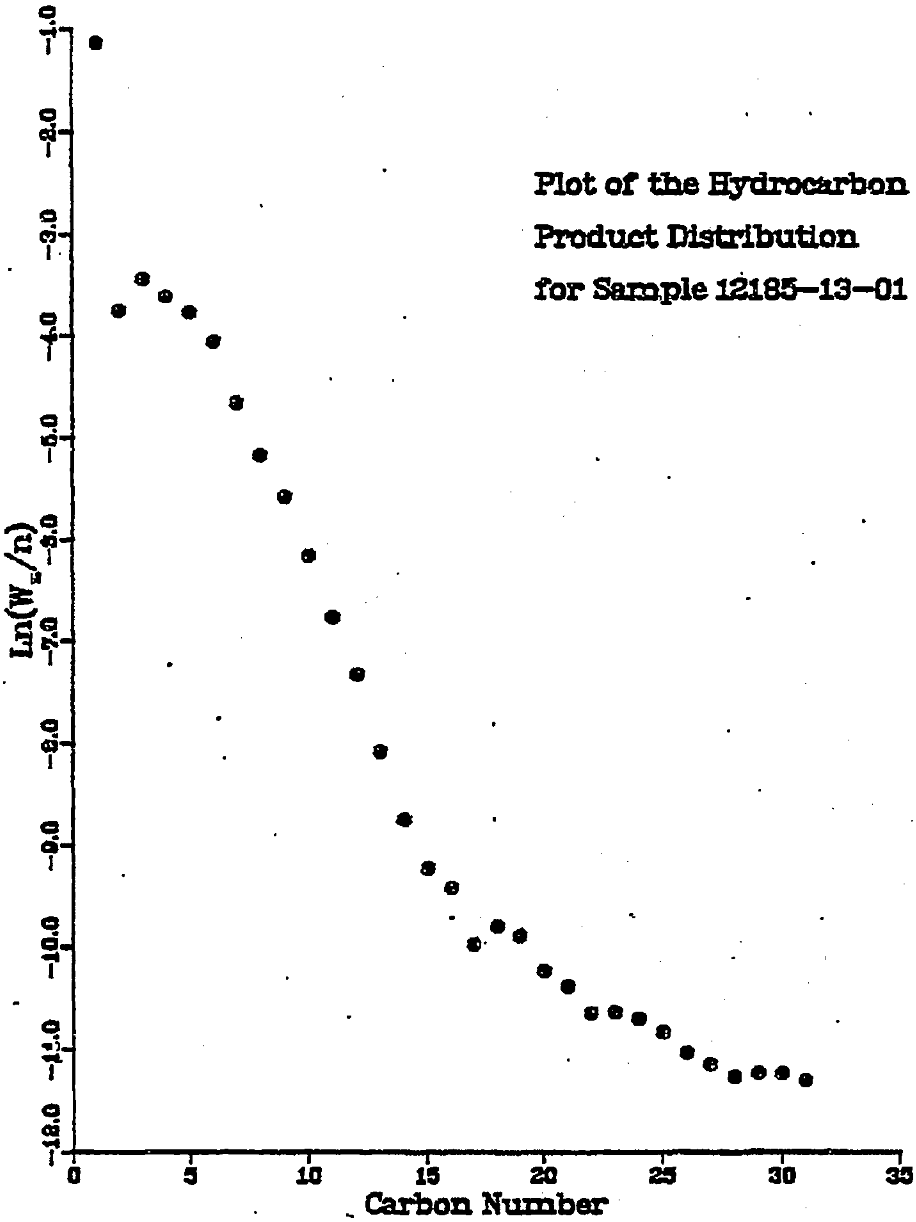

Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. B318



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

Fig. B319



Plot of the Hydrocarbon
Product Distribution
for Sample 12185–13–01
Ln(W_n/n)
Carbon Number

Fig. B320

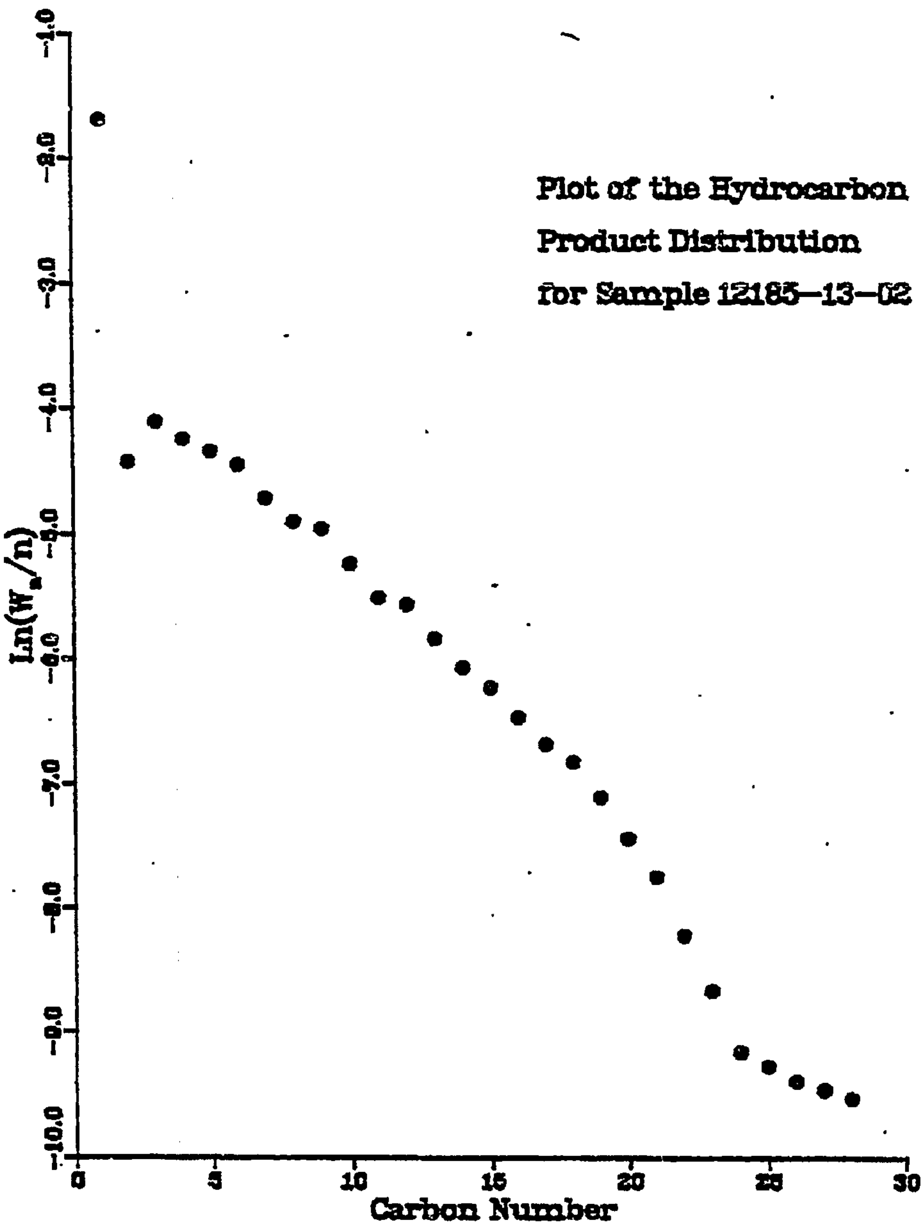

Plot of the Hydrocarbon
Product Distribution
for Sample 12185—13—02
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
Carbon Number

Fig. B321

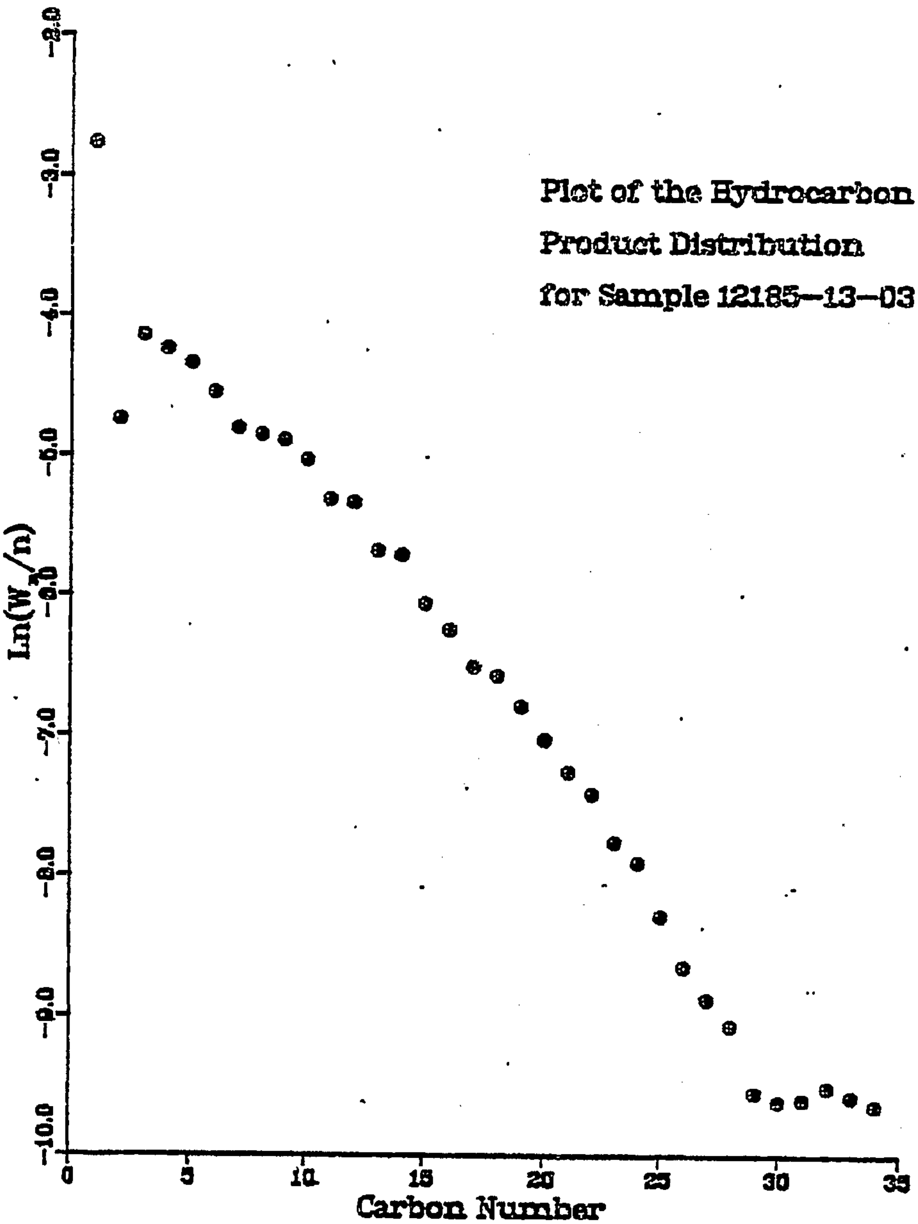
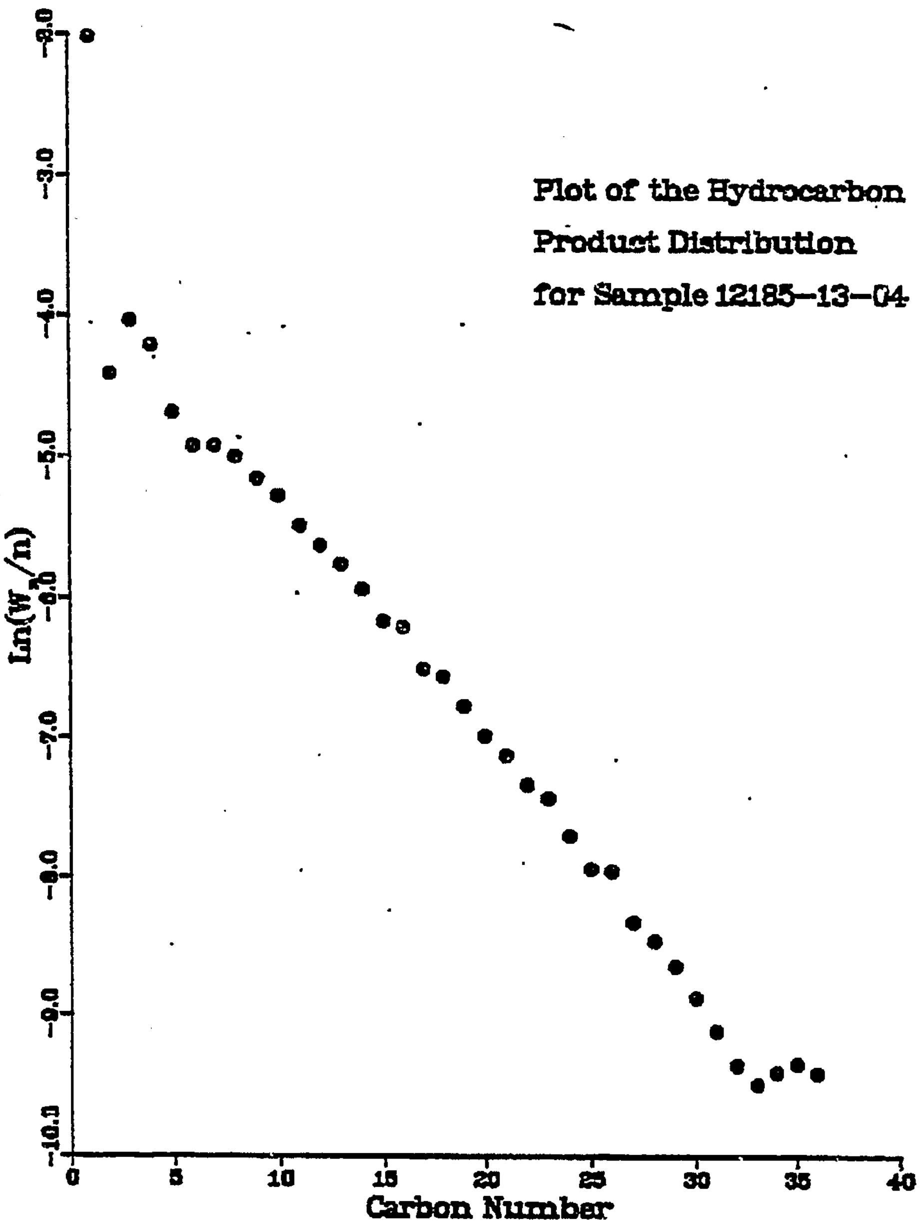

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-13-03
Ln(W/n)
Carbon Number
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35

Fig. B322



Plot of the Hydrocarbon
Product Distribution
for Sample 12185-13-04
Ln(W_n/n)
Carbon Number
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40

Fig. B323

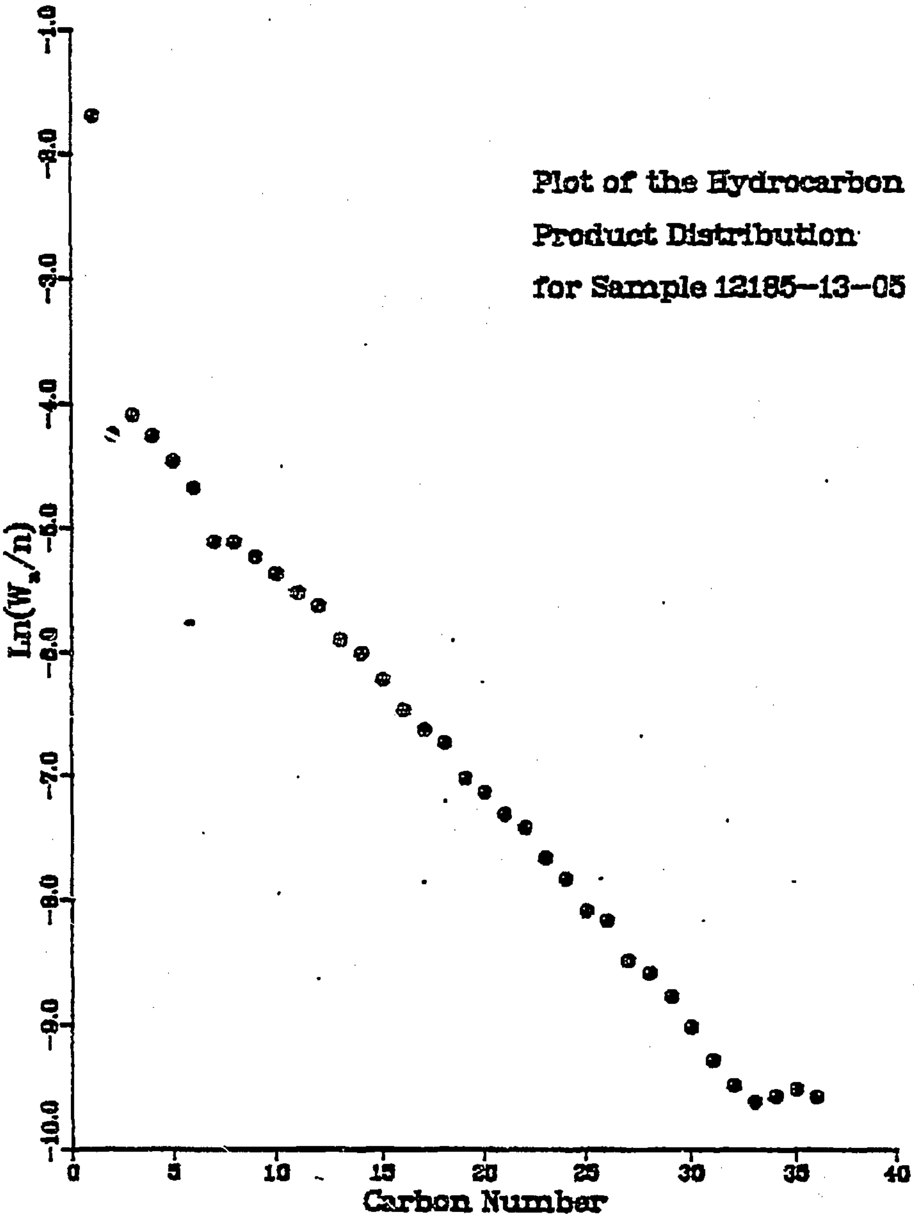

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-13-05
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B324

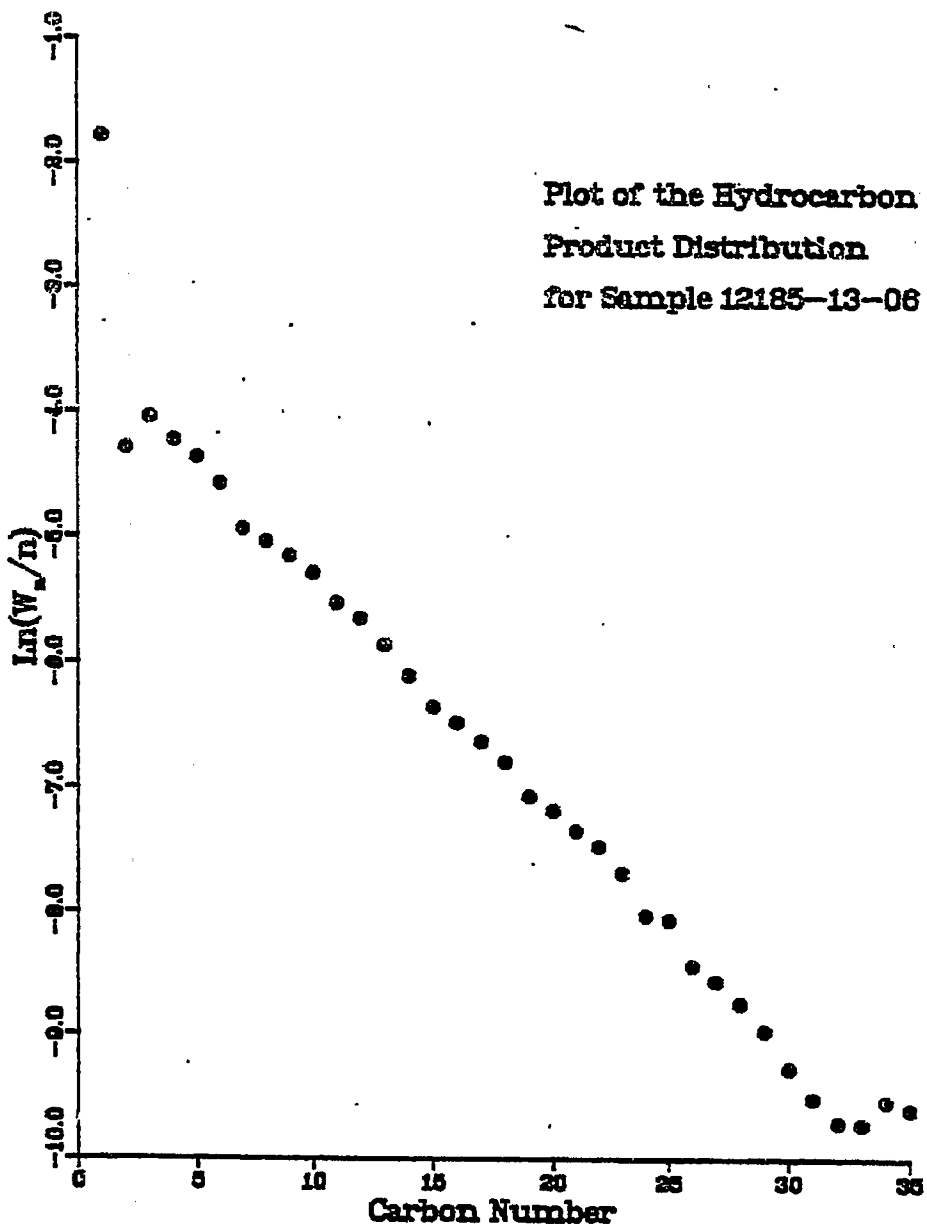

Plot of the Hydrocarbon
Product Distribution
for Sample 12185-13-06
Ln(W_n/n)
Carbon Number
0
5
10
15
20
25
30
35

Fig. B325

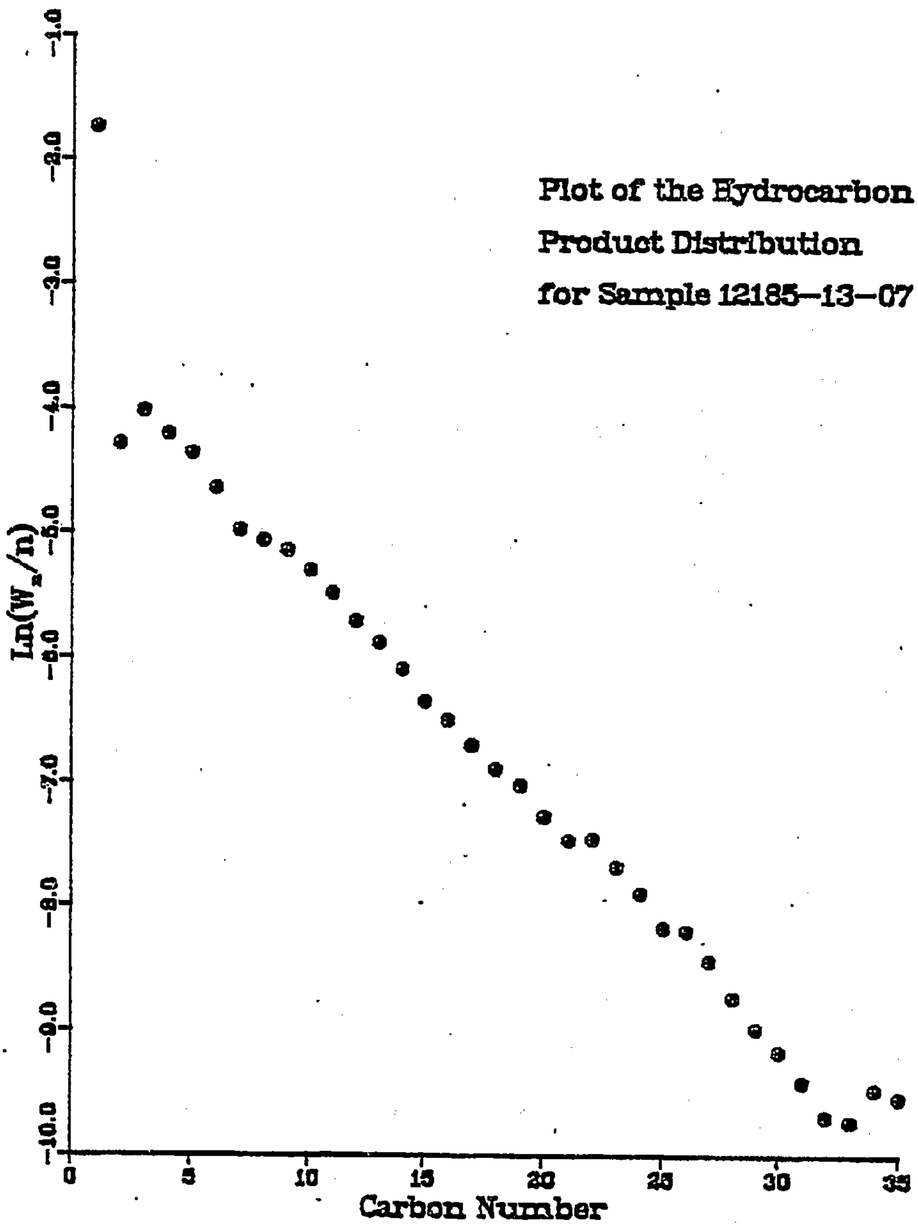
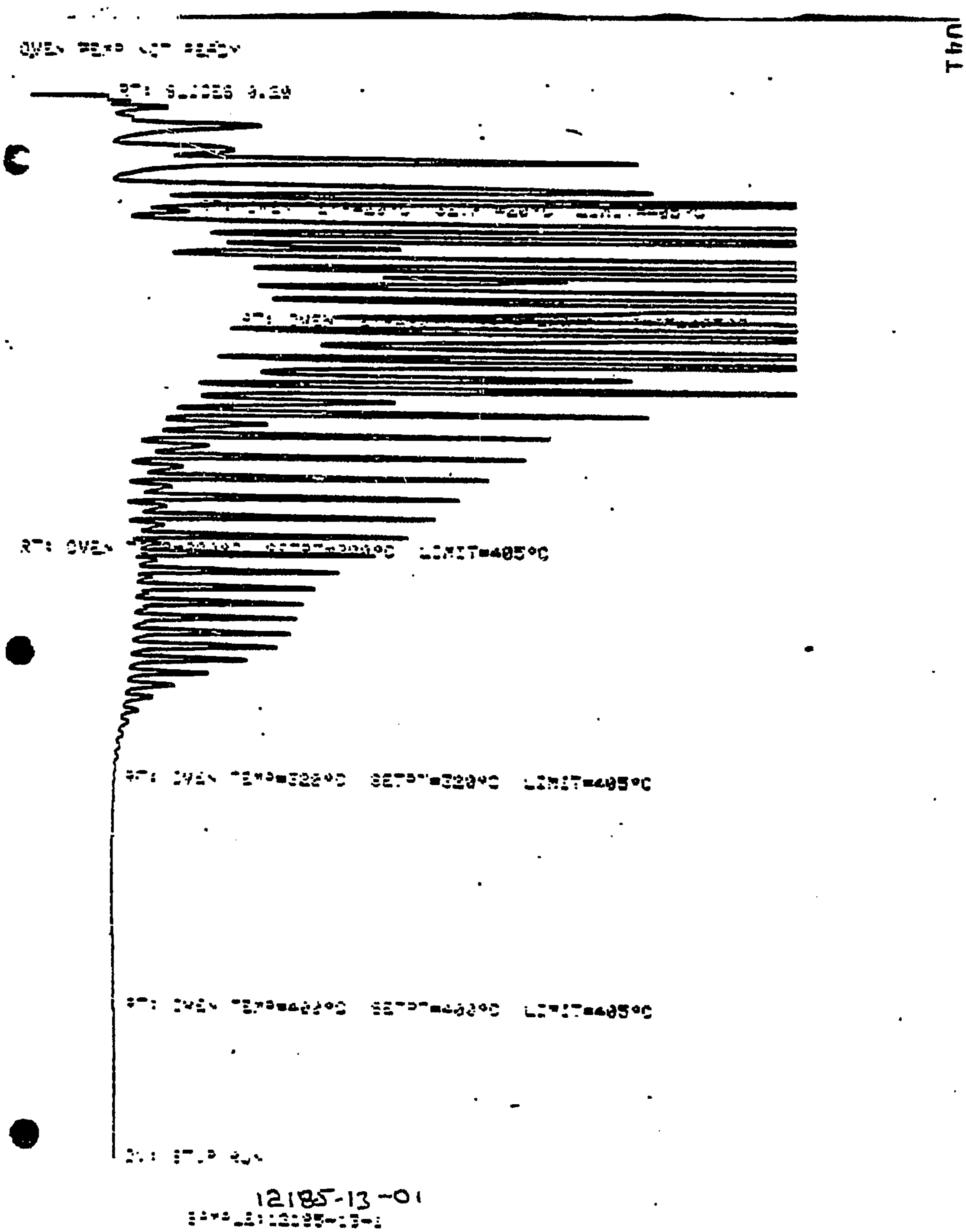
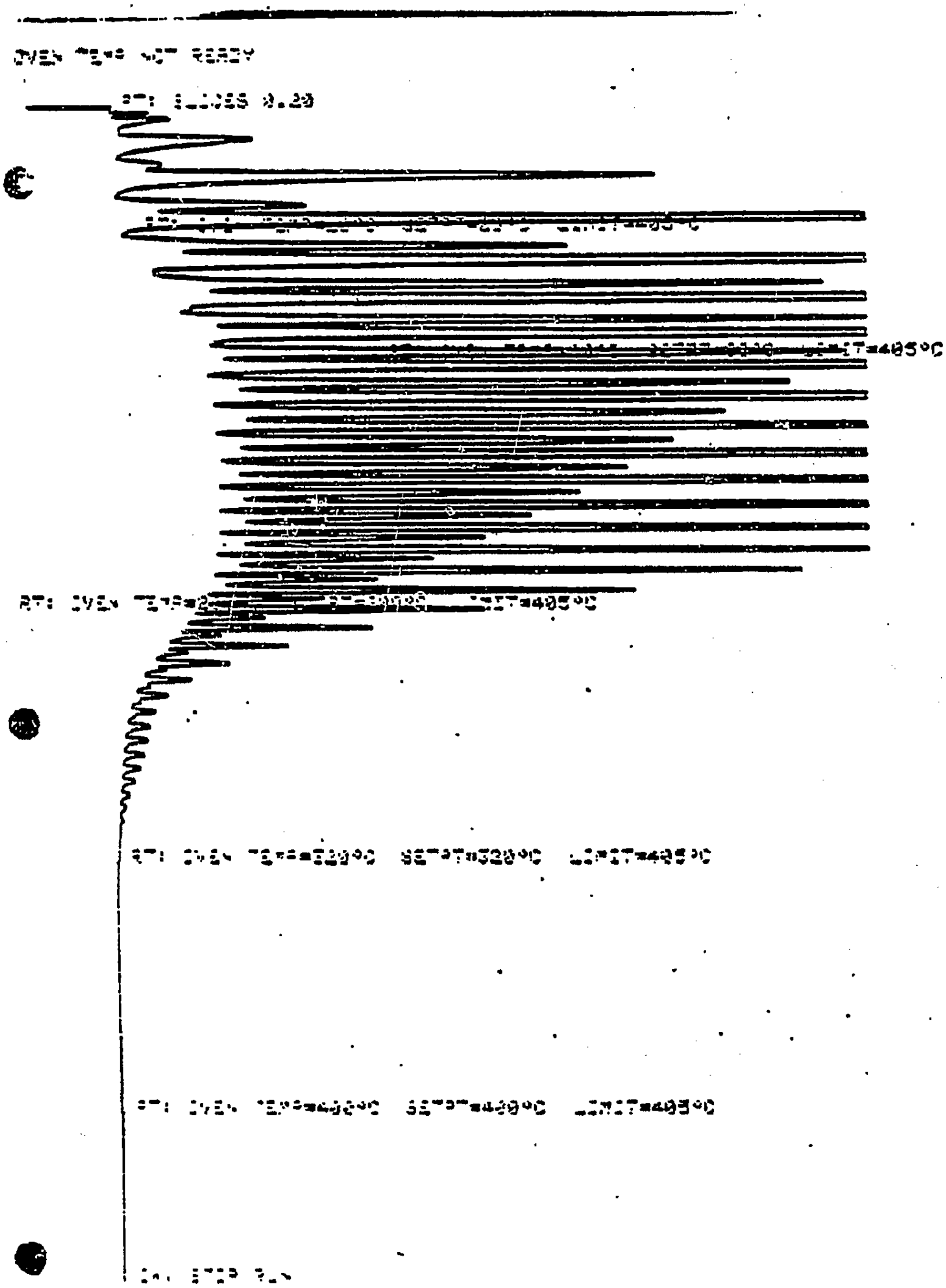

Plot of the Hydrocarbon
Product Distribution
for Sample 12185—13—07
Ln(Wn/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B326



12185-13-01

Fig. B327



12195-13-02

Fig. B328

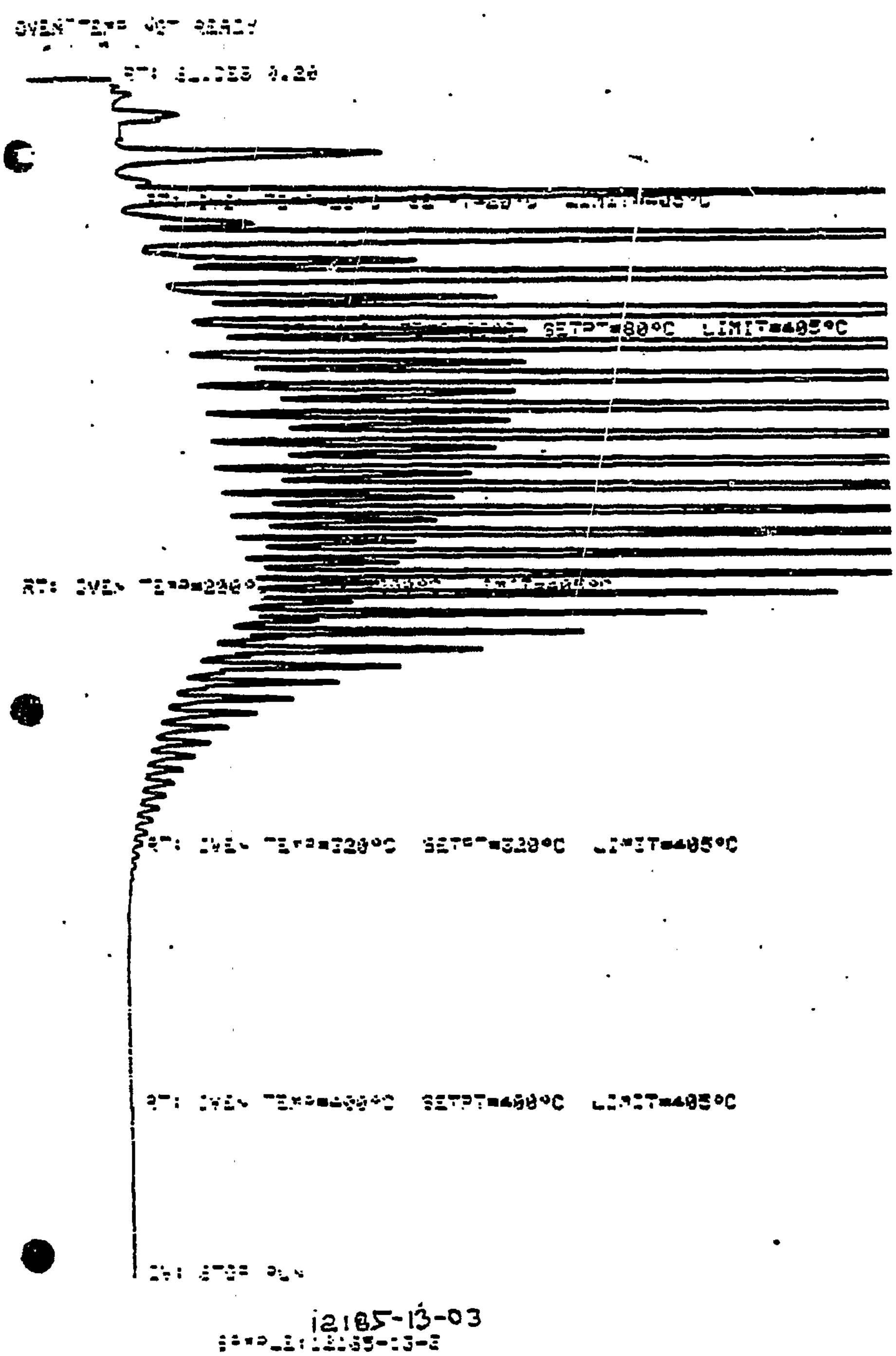
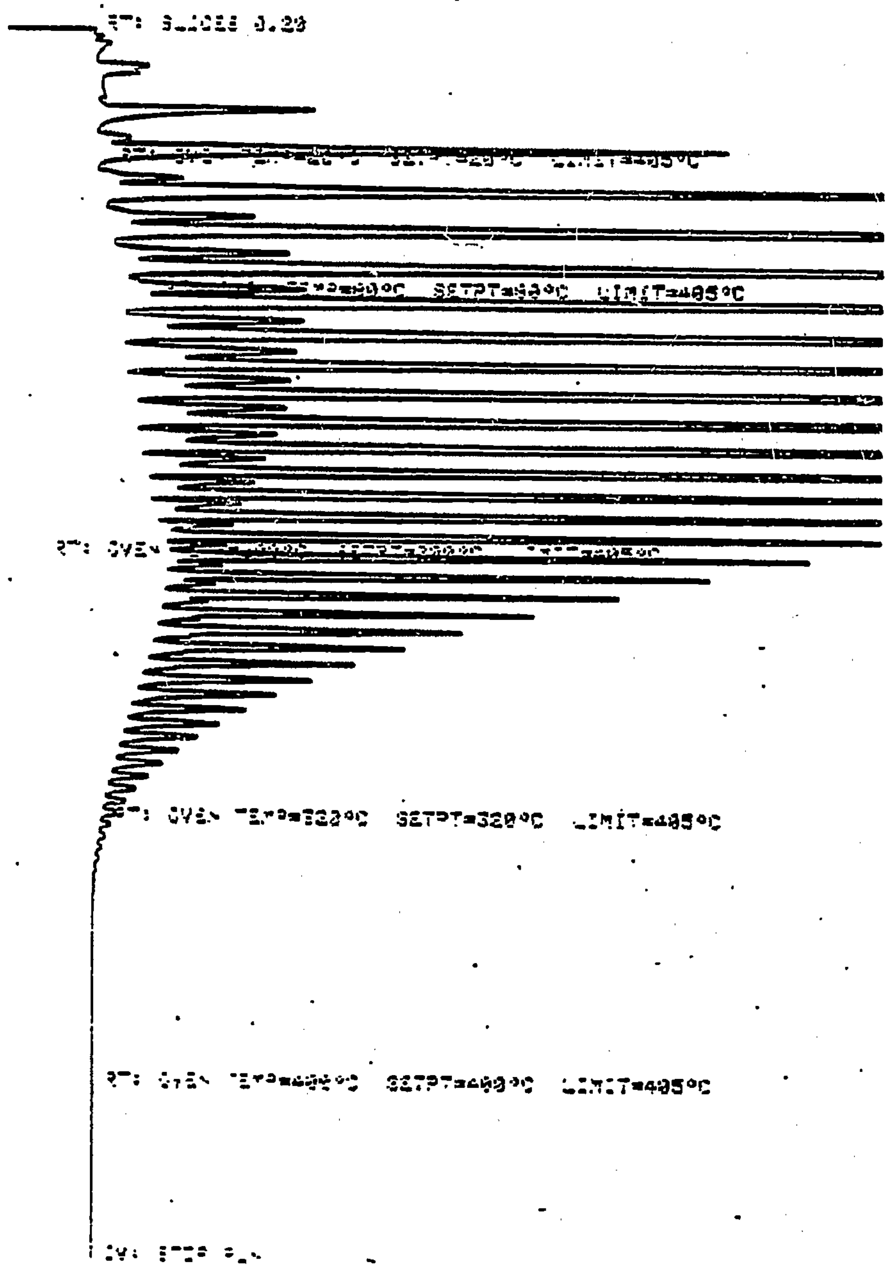


Fig. B329



12185-12-04

Fig. B330

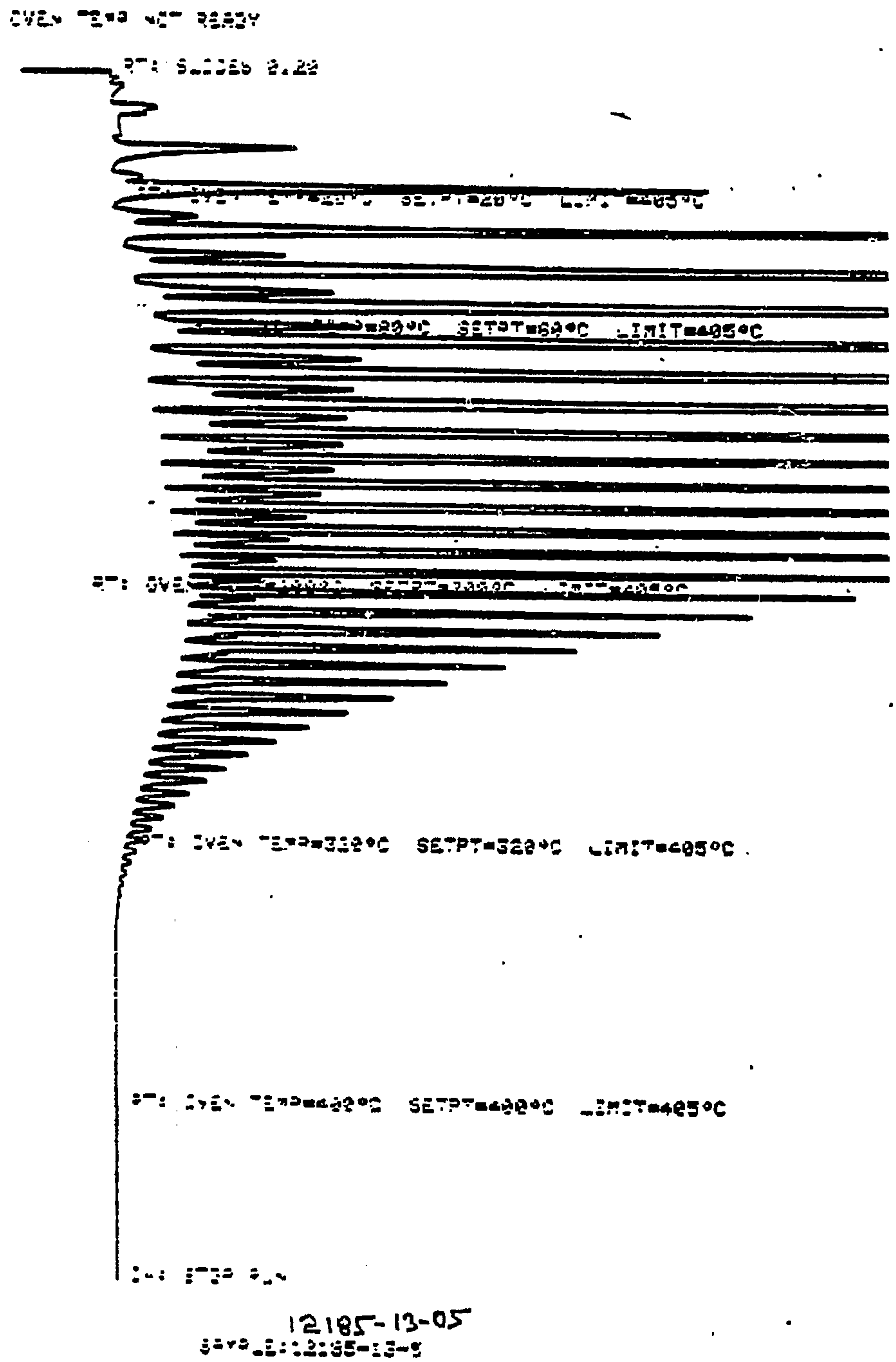


Fig. B331

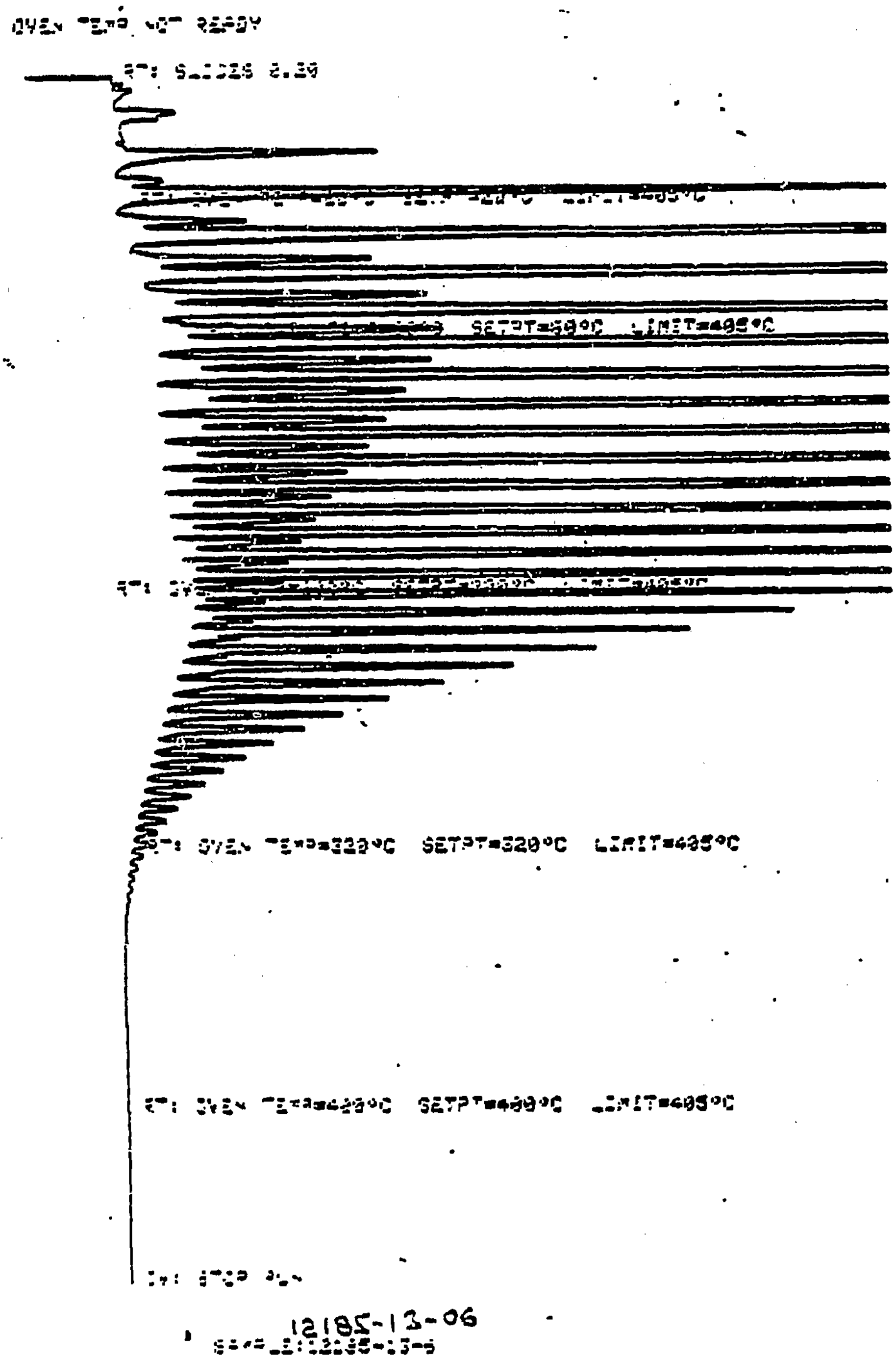
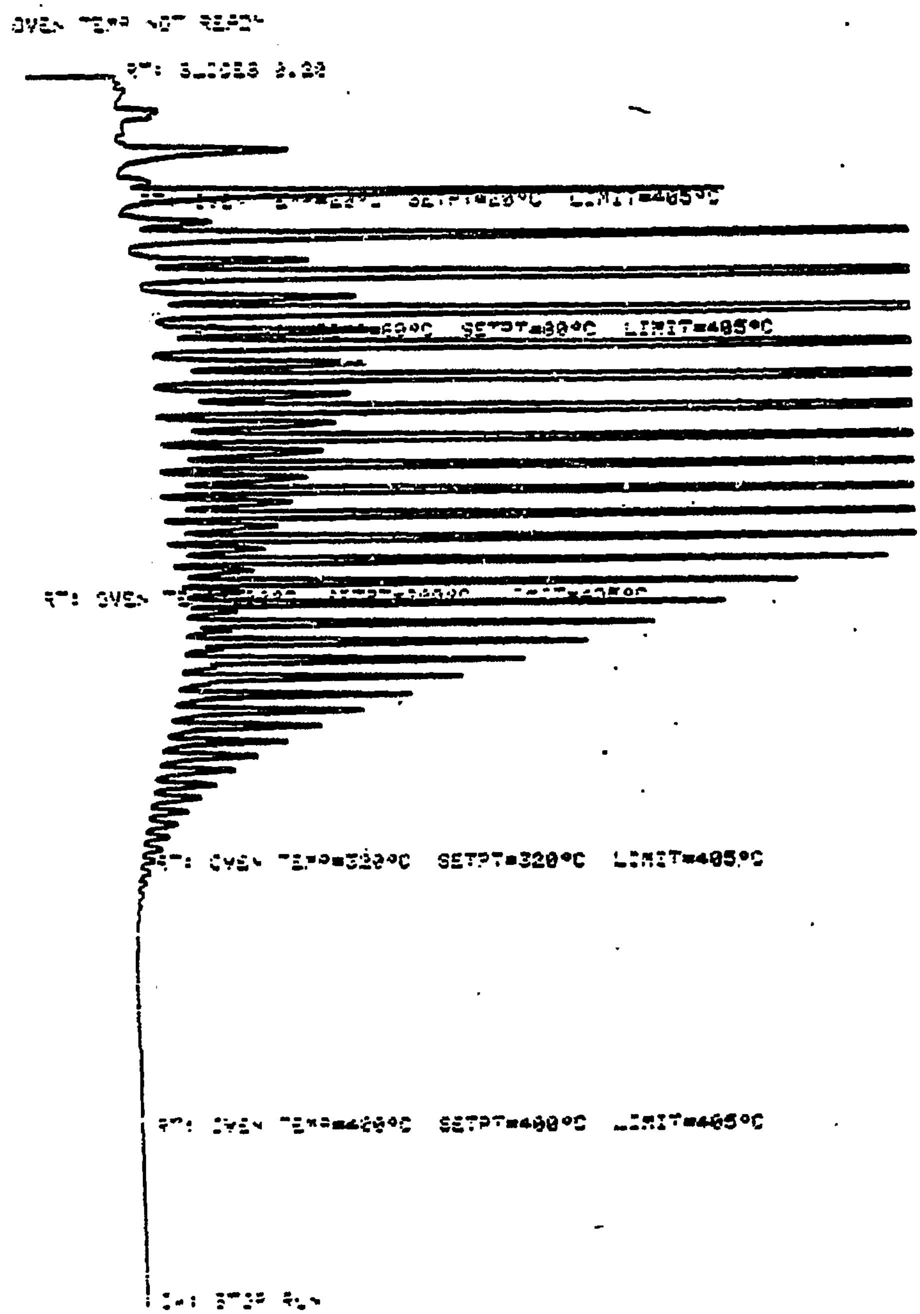


Fig. B332



12185-13-07

Fig. B333

RESULT OF SYNGAS OPERATION

RUN NO. 12185-13
CATALYST CO/X9/X10-U113 12251-43 80 CC 34.1 G (WT CHANGE +14 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-13-01	185-13-02	185-13-03	185-13-04	185-13-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.5	42.5	66.5	90.5	114.5
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	263	266	255	263	261
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	18.50	24.00	24.00	24.00	24.00
EFFLNT GAS LITER	176.30	173.75	222.10	252.60	297.75
GM AQUEOUS LAYER	23.37	61.67	75.19	69.53	63.90
GM OIL	4.29	42.51	30.56	36.61	27.99
MATERIAL BALANCE					
GM ATOM CARBON %	96.42	92.23	87.78	96.65	94.74
GM ATOM HYDROGEN %	84.88	97.29	84.81	99.53	104.23
GM ATOM OXYGEN %	106.90	96.71	100.52	103.10	100.50
RATIO CHX/(H2O+CO2)	0.8104	0.9182	0.7050	0.8551	0.8516
RATIO X IN CHX	2.8243	2.4858	2.2423	2.3923	2.4853
USAGE H2/CO PRODT	0.9360	1.2335	1.9162	1.6505	1.8284
FEED H2/CO FRM EFFLNT	0.8803	1.0549	0.9662	1.0298	1.1001
RESIDUAL H2/CO RATIO	0.4899	0.2764	0.2753	0.4092	0.5707
RATIO CO2/(H2O+CO2)	0.7158	0.4516	0.1507	0.2307	0.1772
K SHIFT IN EFFLNT	1.2341	0.2276	0.0489	0.1227	0.1229
SPECIFIC ACTIVITY SA	11.8014	14.8632	6.2281	2.8946	1.5031
CONVERSION					
ON CO %	87.51	81.34	42.11	49.99	42.09
ON H2 %	93.05	95.11	83.50	80.13	69.96
ON CO+H2 %	90.11	88.41	62.45	65.28	56.69
PRDT SELECTIVITY,WT %					
CH4	32.33	18.38	6.30	13.35	18.31
C2 HC'S	4.72	2.39	1.75	2.42	2.87
C3H8	8.53	3.54	1.66	2.98	3.34
C3H6=	1.10	1.38	3.11	2.34	1.69
C4H10	8.26	3.07	1.86	2.66	3.06
C4H8=	2.59	2.65	3.91	3.28	2.62
C5H12	9.04	3.82	2.63	3.36	3.54
C5H10=	2.48	2.48	3.90	1.22	2.23
C6H14	9.53	4.17	3.24	3.78	3.88
C6H12= & CYCLO'S	0.68	1.50	2.52	0.02	1.37
C7+ IN GAS	13.70	7.47	9.80	8.30	7.81
LIQ HC'S	7.05	49.14	59.34	56.29	49.29
TOTAL	100.00	100.00	100.00	100.00	100.00

Table B24

SUB-GROUPING					
C1 -C4	57.52	31.42	18.58	27.03	31.89
C5 -420 F	38.23	46.23	48.78	38.64	38.29
420-700 F	3.90	21.13	28.96	26.63	23.21
700-END PT	0.35	1.23	3.68	7.71	6.60
C5+-END PT	42.48	68.58	81.42	72.97	68.11
ISO/NORMAL MOLE RATIO					
C4	0.0471	0.0196	0.0205	0.0201	0.0242
C5	0.1497	0.0817	0.0555	0.0732	0.0898
C6	0.4086	0.2043	0.0681	0.0973	0.1325
C4=	0.1708	0.1038	0.0000	0.0000	0.0986
PARAFFIN/OLEFIN RATIO					
C3	7.4014	2.4387	0.5108	1.2147	1.8791
C4	3.0715	1.1170	0.4592	0.7817	1.1281
C5	3.5460	1.4968	0.6552	2.6723	1.5465
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7076	0.7889	0.8197	0.8461	0.8362
RATIO CH4/(1-A)**2	3.7813	4.1238	1.9378	5.6383	6.8253
ALPHA FRM CORRELATION	0.8454	0.8731	0.8739	0.8542	0.8381
ALPHA (EXPTL/CORR)	0.8370	0.9035	0.9380	0.9906	0.9978
WTCH4 FRM CORRELATION	16.4035	8.4250	5.8673	13.6847	18.2599
WTCH4 (EXPTL/CORR)	1.9707	2.1822	1.0733	0.9758	1.0025
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL	OIL WAX	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.7218*	0.7321*	0.7442*	0.7490*	0.7485*
N, REFRACTIVE INDEX	1.4095*	1.4147*	1.4198*	1.4209*	1.4211*
SIMULT'D DISTILATN					
10 WT % @ DEG F	209	235	259	282	293
16	247	257	300	303	319
50	341	407	448	481	478
84	482	570	624	683	678
90	589	614	676	734	731
RANGE(16-84 %)	235	313	324	380	359
WT % @ 420 F	39.70	54.50	45.00	39.00	39.50
WT % @ 700 F	95.00	97.50	93.80	86.30	86.60
	75.67	54.50	45.00	39.00	39.50
	95.04	97.52	92.33	86.30	86.57

Table B24, cont

RESULT OF SYNGAS OPERATION

RUN NO. 12185-13
CATALYST CO/X9/X10-U113 12251-43 80 CC 34.1 G (WT CHANGE +14.0 G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12185-13-06	185-13-07
FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	140.0	162.5
PRESSURE,PSIG	300	300
TEMP. C	260	260
FEED CC/MIN	400	400
HOURS FEEDING	25.50	22.50
EFFLNT GAS LITER	319.30	283.20
GM AQUEOUS LAYER	63.79	57.69
GM OIL	29.42	25.29
MATERIAL BALANCE		
GM ATOM CARBON %	95.76	95.64
GM ATOM HYDROGEN %	102.23	103.04
GM ATOM OXYGEN %	99.91	100.50
RATIO CHX/(H2O+CO2)	0.8884	0.8706
RATIO X IN CHX	2.4588	2.4741
USAGE H2/CO PRODT	1.7660	1.8058
FEED H2/CO FRM EFFLNT	1.0675	1.0773
RESIDUAL H2/CO RATIO	0.5663	0.5653
RATIO CO2/(H2O+CO2)	0.1892	0.1799
K SHIFT IN EFFLNT	0.1321	0.1240
SPECIFIC ACTIVITY SA	1.6024	1.5726
CONVERSION		
ON CO %	41.78	41.27
ON H2 %	69.11	69.18
ON CO+H2 %	55.89	55.75
PRDT SELECTIVITY,WT %		
CH4	16.71	17.54
C2 HC'S	2.75	2.77
C3H8	3.51	3.55
C3H6=	1.77	1.85
C4H10	3.14	3.18
C4H8=	2.71	2.81
C5H12	3.86	3.89
C5H10=	2.49	2.54
C6H14	4.20	4.27
C6H12= & CYCLO'S	1.46	0.99
C7+ IN GAS	8.51	8.63
LIQ HC'S	48.89	47.97
TOTAL	100.00	100.00

Table B25

SUB-GROUPING		
C1 -C4	30.59	31.70
C5 -420 F	41.54	40.95
420-700 F	22.19	21.35
700-END PT	5.67	6.00
C5+-END PT	69.41	68.30
ISO/NORMAL MOLE RATIO		
C4	0.0193	0.0204
C5	0.0767	0.0843
C6	0.1108	0.1156
C4=	0.0789	0.0790
PARAFFIN/OLEFIN RATIO		
C3	1.8886	1.8301
C4	1.1164	1.0943
C5	1.5096	1.4891
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))	0.8289	0.8306
RATIO CH4/(1-A)**2	5.7075	6.1098
ALPHA FRM CORRELATION	0.8385	0.8386
ALPHA (EXPTL/CORR)	0.9885	0.9904
WTCH4 FRM CORRELATION	17.9164	17.8904
WTCH4 (EXPTL/CORR)	0.9329	0.9805
LIQ HC COLLECTION		
PHYS. APPEARANCE	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.7448*	0.7449*
N, REFRACTIVE INDEX	1.4190*	1.4187*
SIMULT'D DISTILATN		
10 WT % @ DEG F	261	274
16	301	300
50	452	451
84	665	668
90	715	725
RANGE(16-84 %)	364	368
WT % @ 420 F	43.00	43.00
WT % @ 700 F	88.40	87.50
	43.00	43.00
	88.36	87.50

Table B25, cont

XVI. Run 25 (12200-14) with Catalyst 25 ($Co/X_9/X_{10}/X_4$/UCC-103)

The purpose of this run was to test an X_4 additive obtained from still another source than those used in Catalysts 16, 19 and 23. All three of those tests failed to produce an active catalyst, and there is reason to suspect that contamination of the X_4 at its source may have been the cause.

Formulation of the catalyst was similar to that of Catalyst 23. The UCC-103 was combined with X_4 (from the new source) before forming in close contact, by the method used in Run 11, with cobalt oxide which had been promoted with X_9 and X_{10}. The resulting powder, after bonding with 15 percent silica, was extruded to 1/8-inch pellets. The final catalyst contained 7.2 percent cobalt, 0.32 percent X_9, 0.43 percent X_{10} and 0.33 percent X_4.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. B334-337. Simulated distillations of the C_5^+ product are plotted in Figs. B338-343. Carbon number product distributions are plotted in Figs. B344-349. Chromatograms from simulated distillations are reproduced in Figs. B350-355. Detailed material balances appear in Tables B26-27.

The initial conversion of syngas was 67.9 percent, with a specific activity of 6.8. This is the highest initial activity yet obtained with an X_4-containing catalyst formulated by the new method first tested in Catalyst 11; the highest specific activity previously obtained was 1.0. Also worth noting is the fact that whereas the other catalysts contained more than 11 percent cobalt, this one contained only 7.2 percent. Estimating the specific activity on a basis of percent cobalt, this catalyst was as active as Catalyst 11 which contained no promoters.

Again, however, the stability was poor. By 140 hours on stream the conversion had dropped to 52.6 percent, with a specific activity of 1.5. The combination of additives X_9, X_{10} and X_4 did not confer the same stabilizing effect in this formulation as it did in Catalyst 15, which was formulated by the previous method.

The product selectivity was unstable as well. The initial methane production was a low 6.5 percent as against 27.5 percent with Catalyst 20, the latter value resulting from a much higher water gas shift activity (60 percent for Catalyst 20, 21 percent for this catalyst).

The olefin content of the C_4's ranged from 60 to 70 percent, as against 35 to 58 percent for Catalyst 20. This was consonant with previous experience that the presence of X_4 raises the olefin content of the lighter products.

The Schulz-Flory plots of the product distribution are linear except for the usual excess of methane, with no evidence of a carbon number cutoff such as observed for Catalyst 20.

This run, with its high initial activity, has been the first successful attempt at incorporating X_4 into this new catalyst formulation. Like the others in its group, however, it suffers from very poor stability.

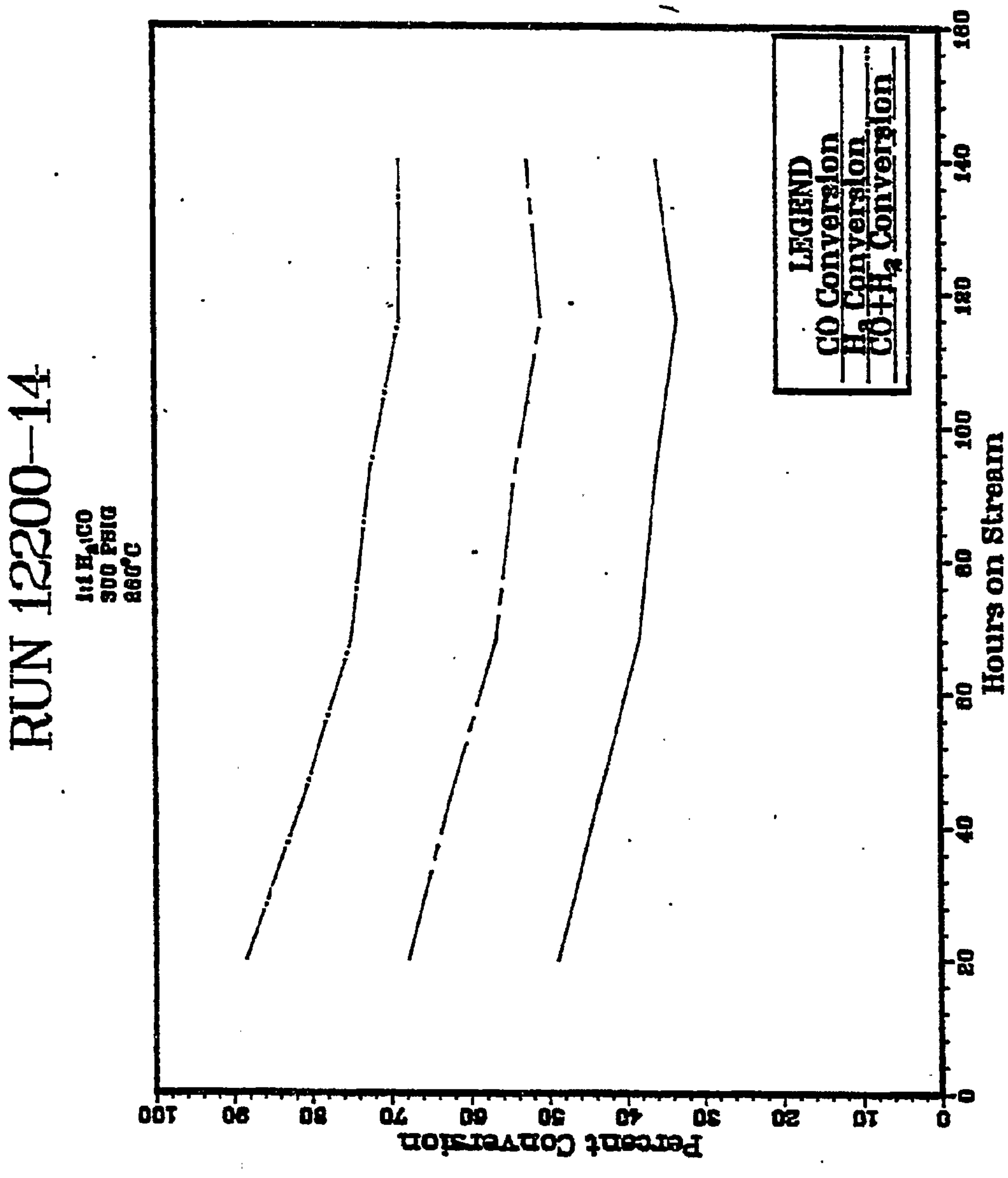

RUN 12200-14
1:1 H2:CO
300 PSIG
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Hours on Stream
Percent Conversion
0
10
20
30
40
50
60
70
80
90
100
120
140
160

Fig. B334

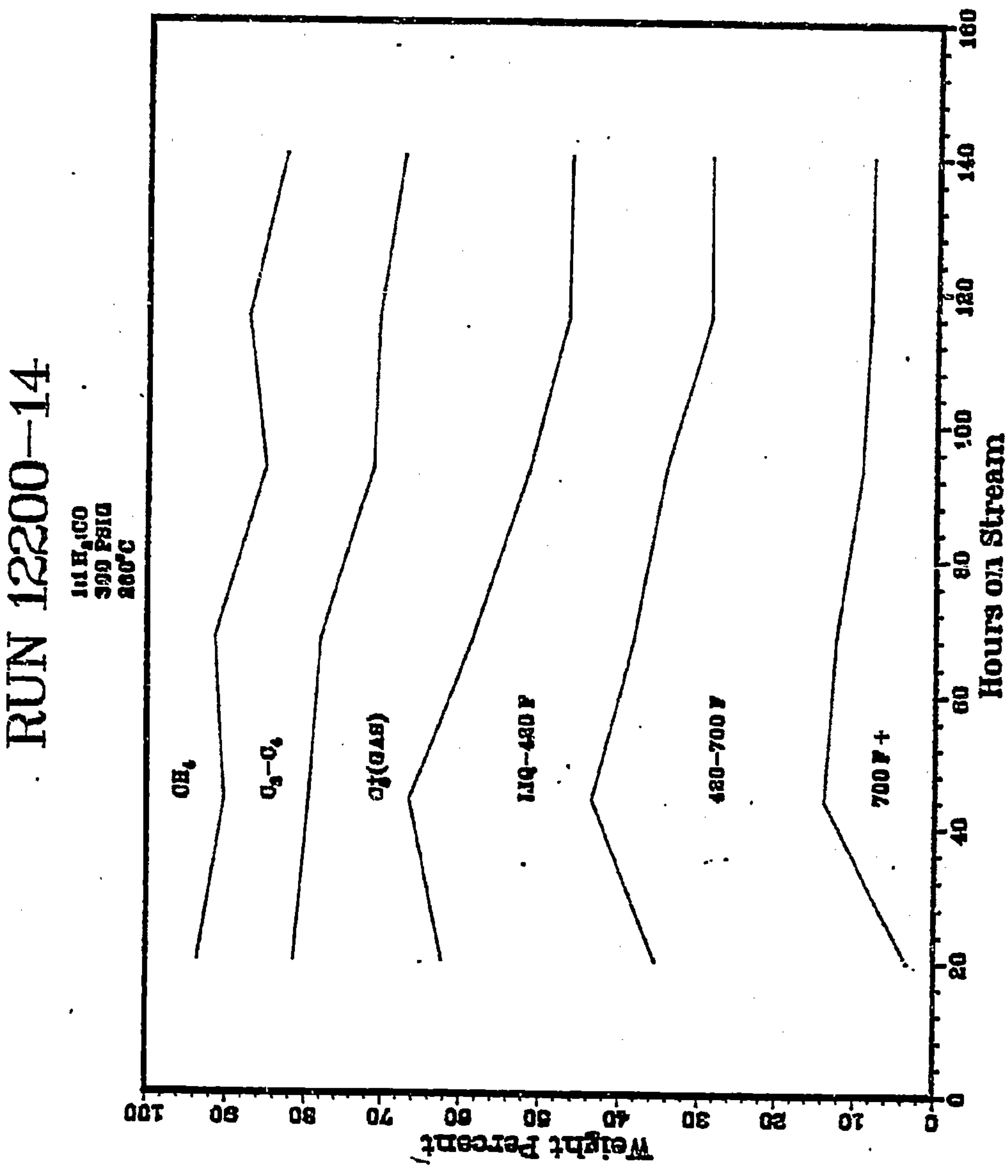

RUN 12200-14
1:1 H$_2$:CO
300 PSIG
260°C
CH$_4$
C$_2$-C$_4$
C$_5$+(GAS)
LIQ-420 F
420-700 F
700 F +
Hours on Stream
Weight Percent

Fig. B335

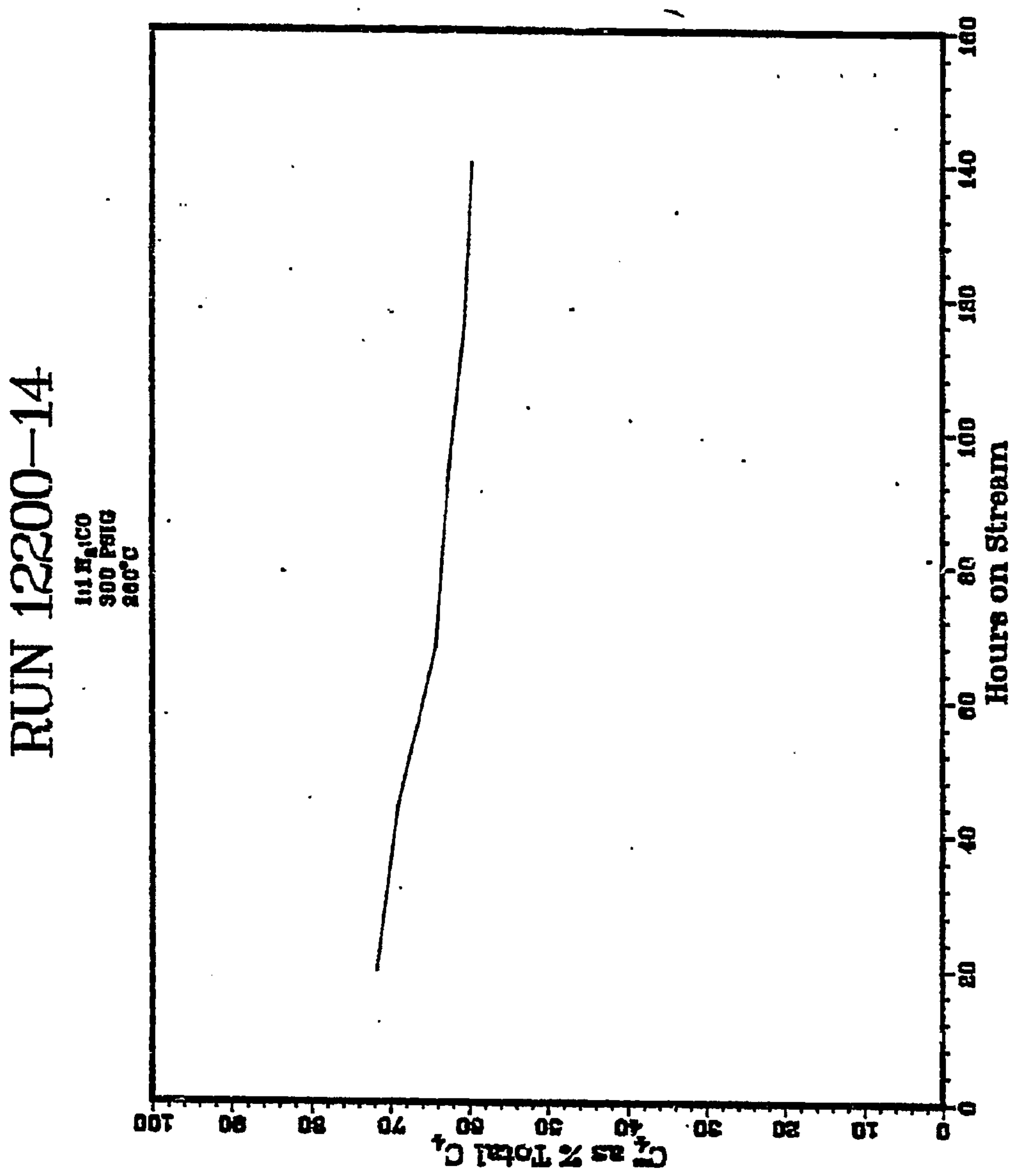

RUN 12200—14
300 PSIG
Hours on Stream
0
20
40
60
80
100
120
140
160
0
10
20
30
40
50
60
70
80
90
100
C₄⁼ as % Total C₄

Fig. B336

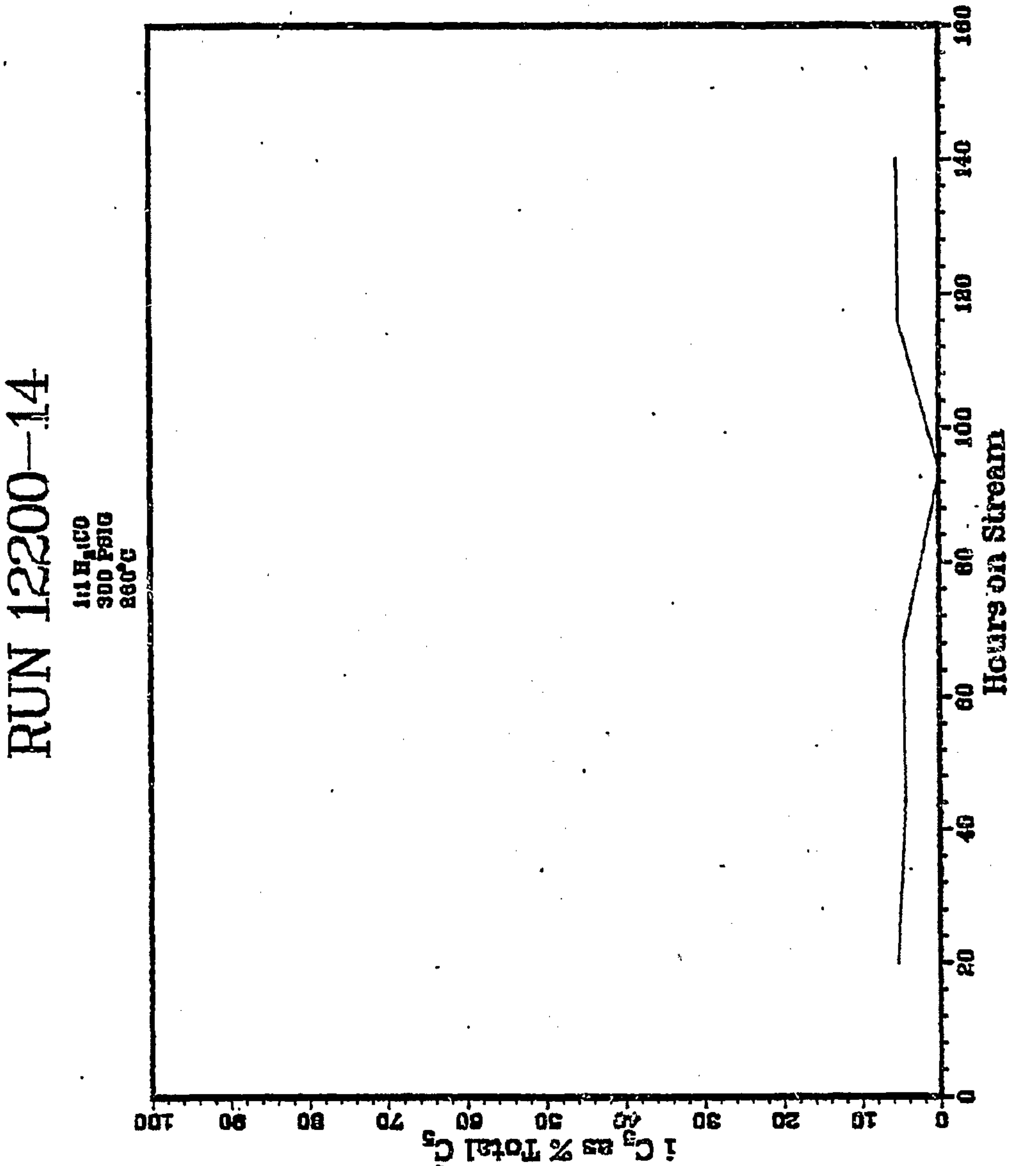


Fig. B337

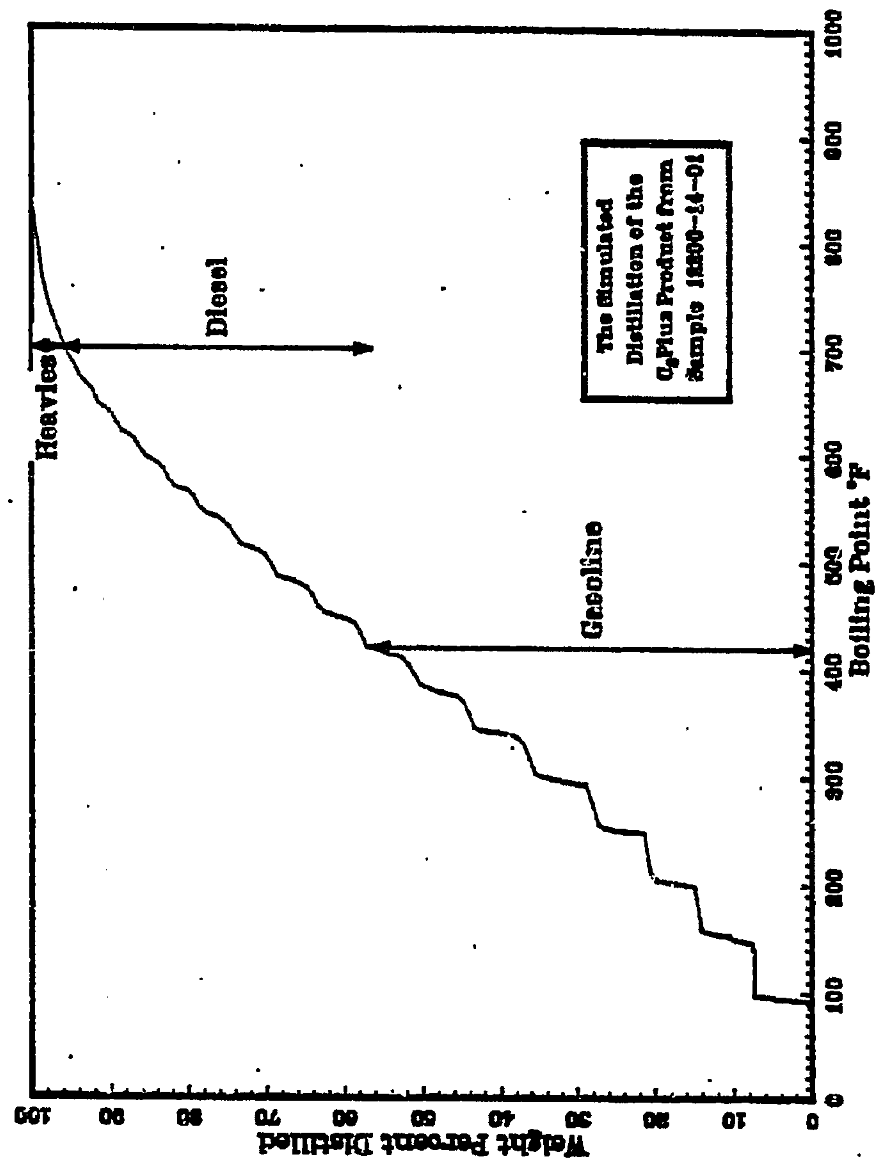

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
Weight Percent Distilled
Boiling Point °F

Fig. B338

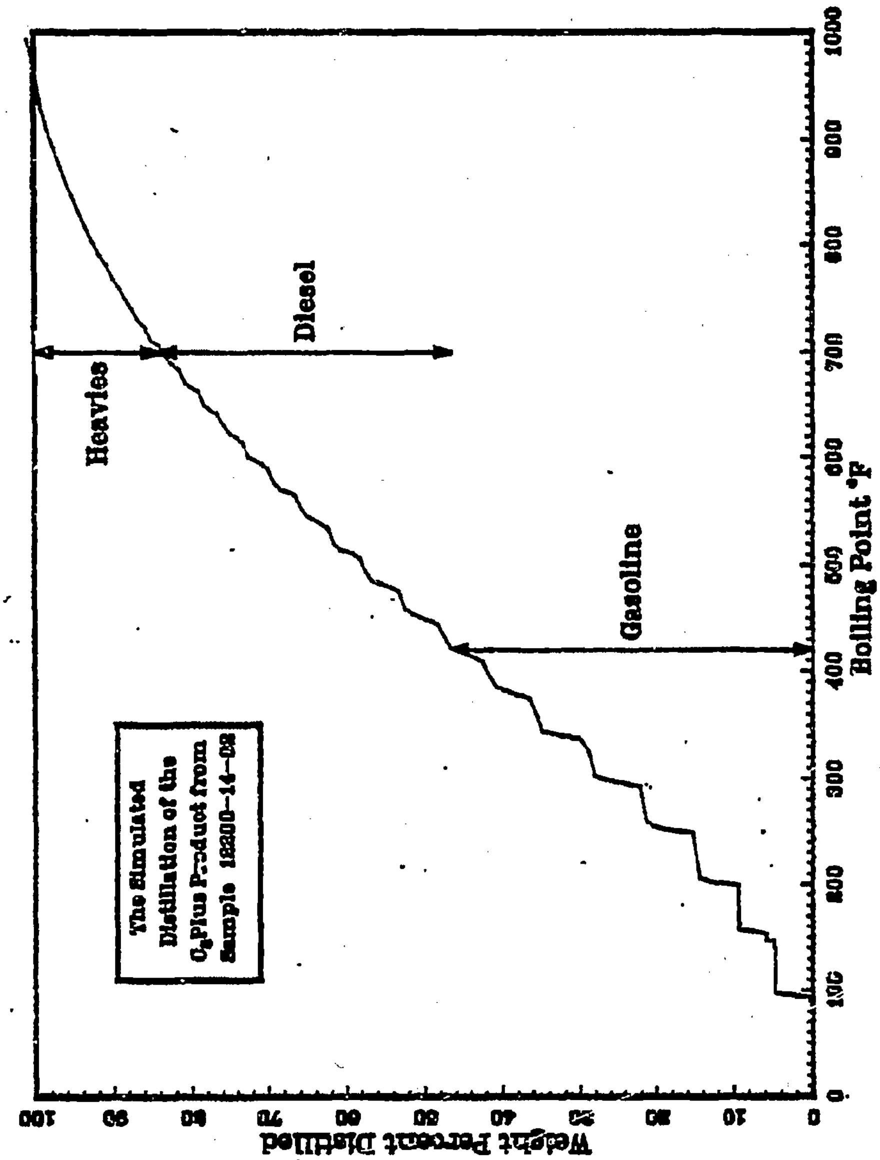

Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. B339

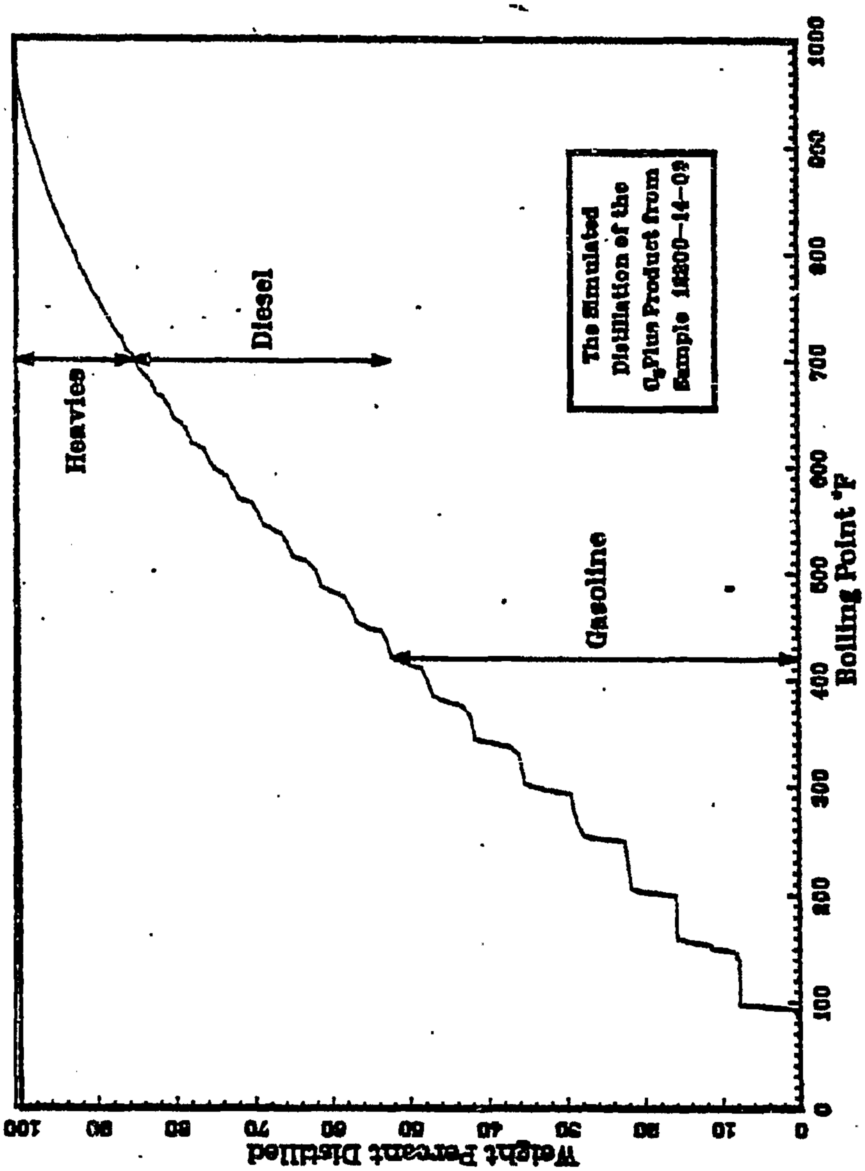

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C_5 Plus Product from
Sample
Boiling Point °F
Weight Percent Distilled

Fig. B340

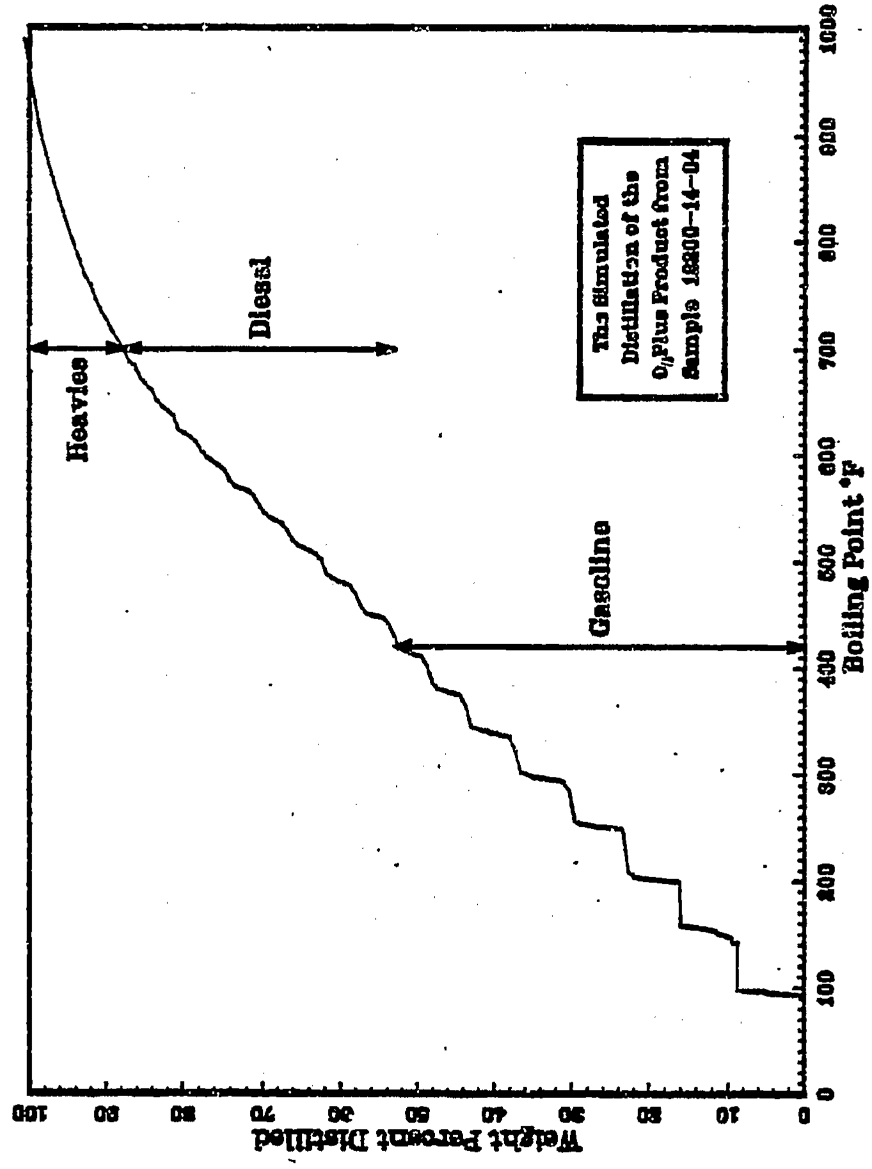

Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. B341

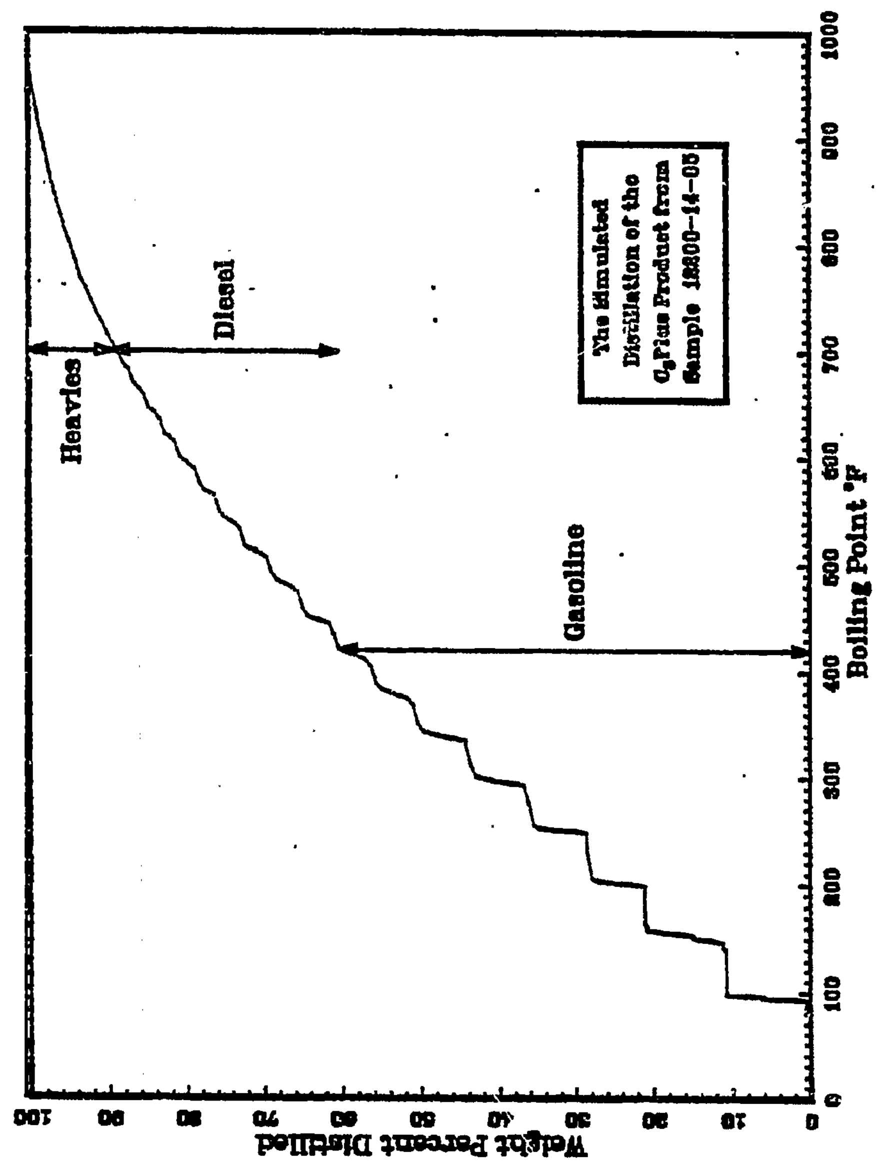

Heavies
Diesel
Gasoline
Boiling Point °F
Weight Percent Distilled

Fig. B342

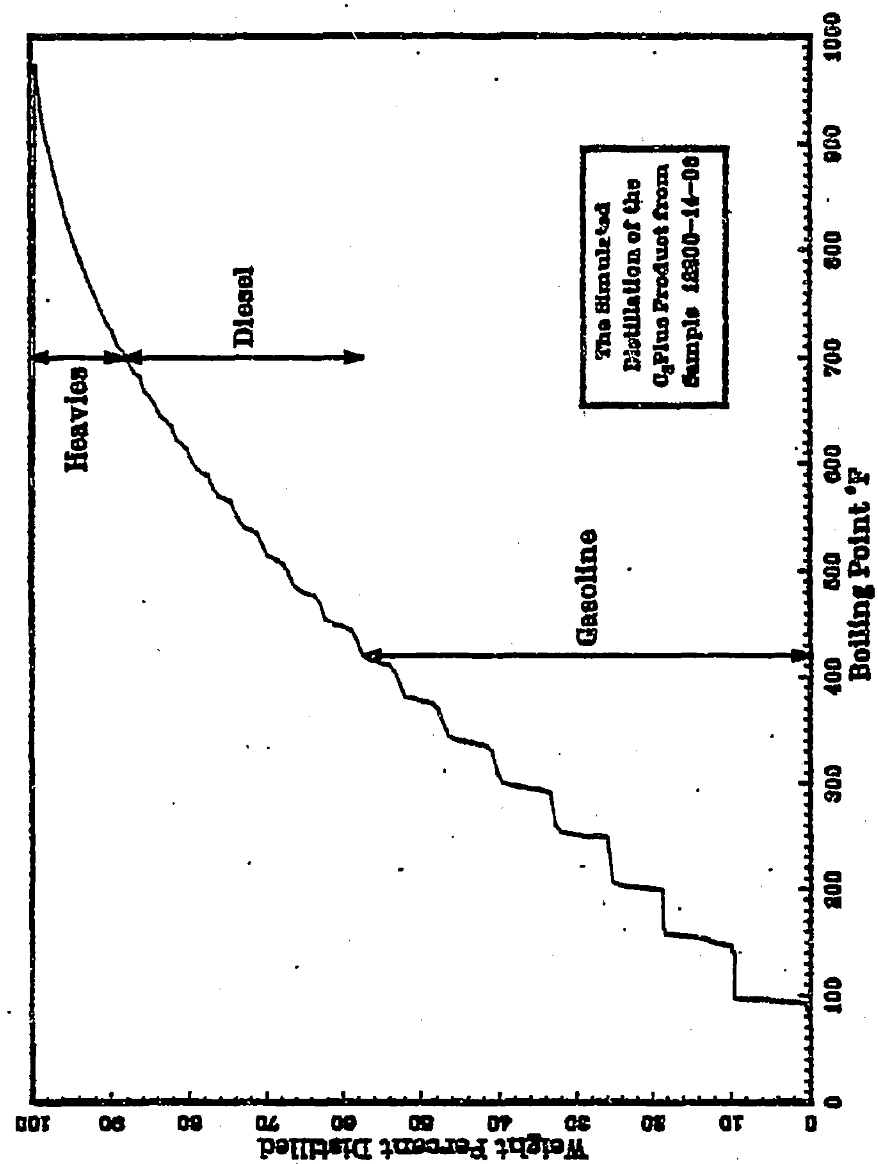
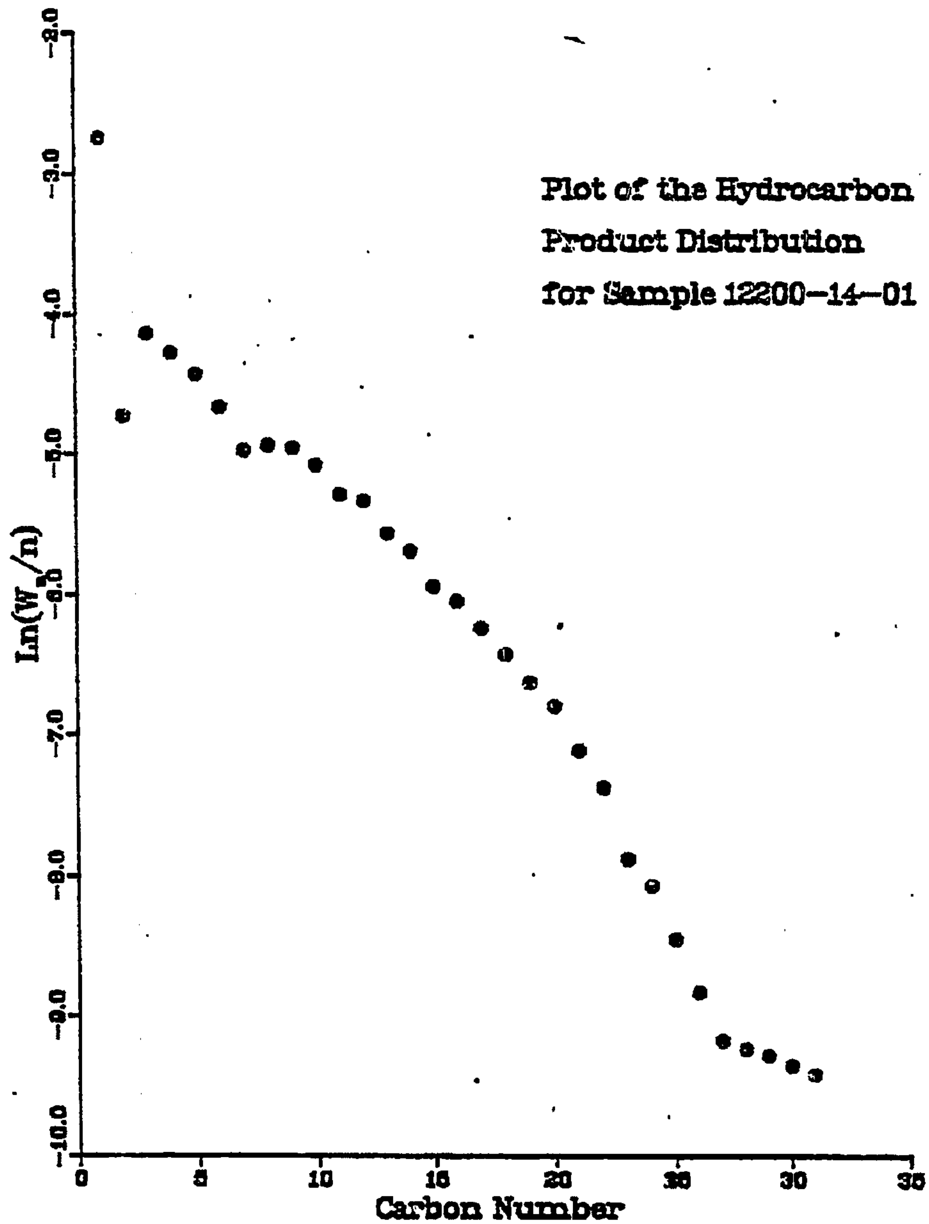
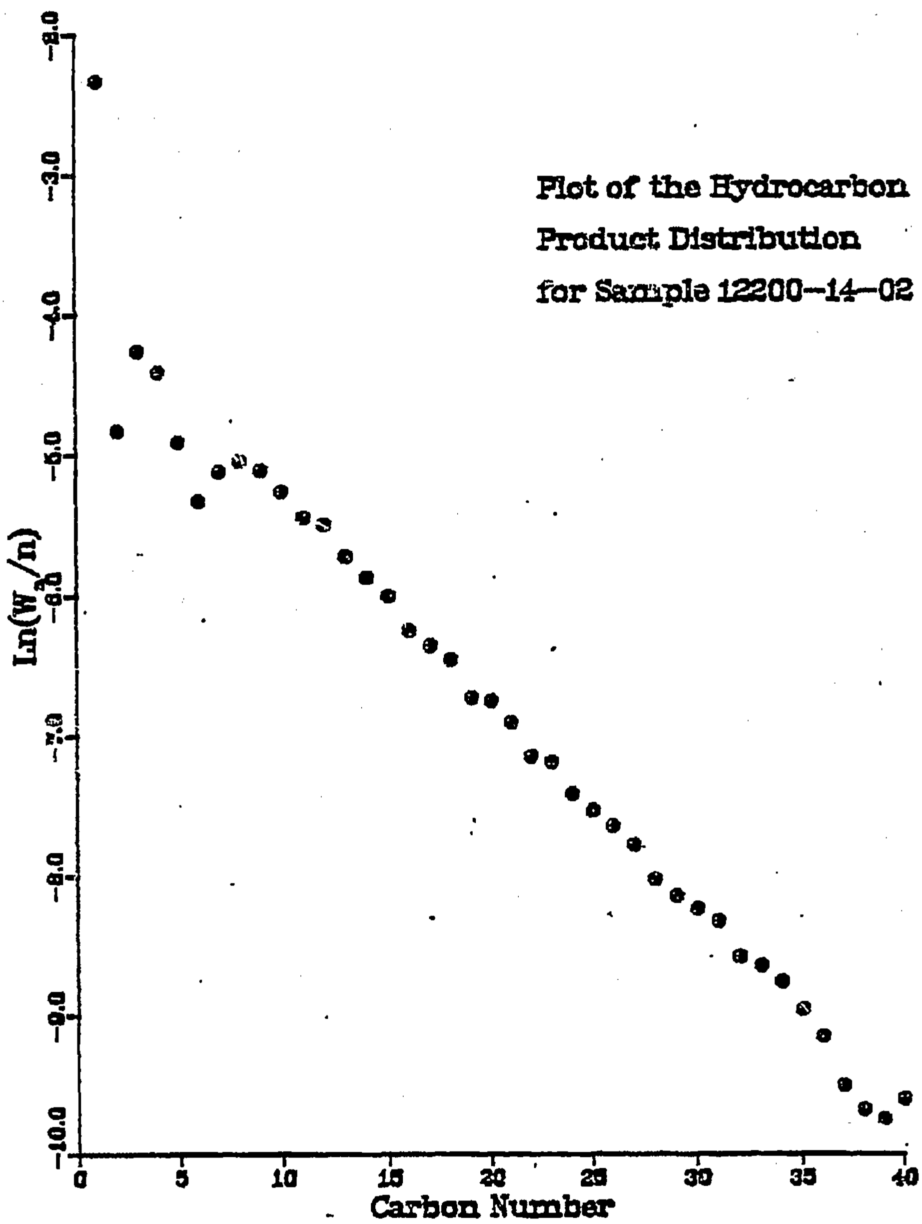

Heavies
Diesel
Gasoline
The Simulated
Distillation of the
C5Plus Product from
Boiling Point °F
Weight Percent Distilled

Fig. B343



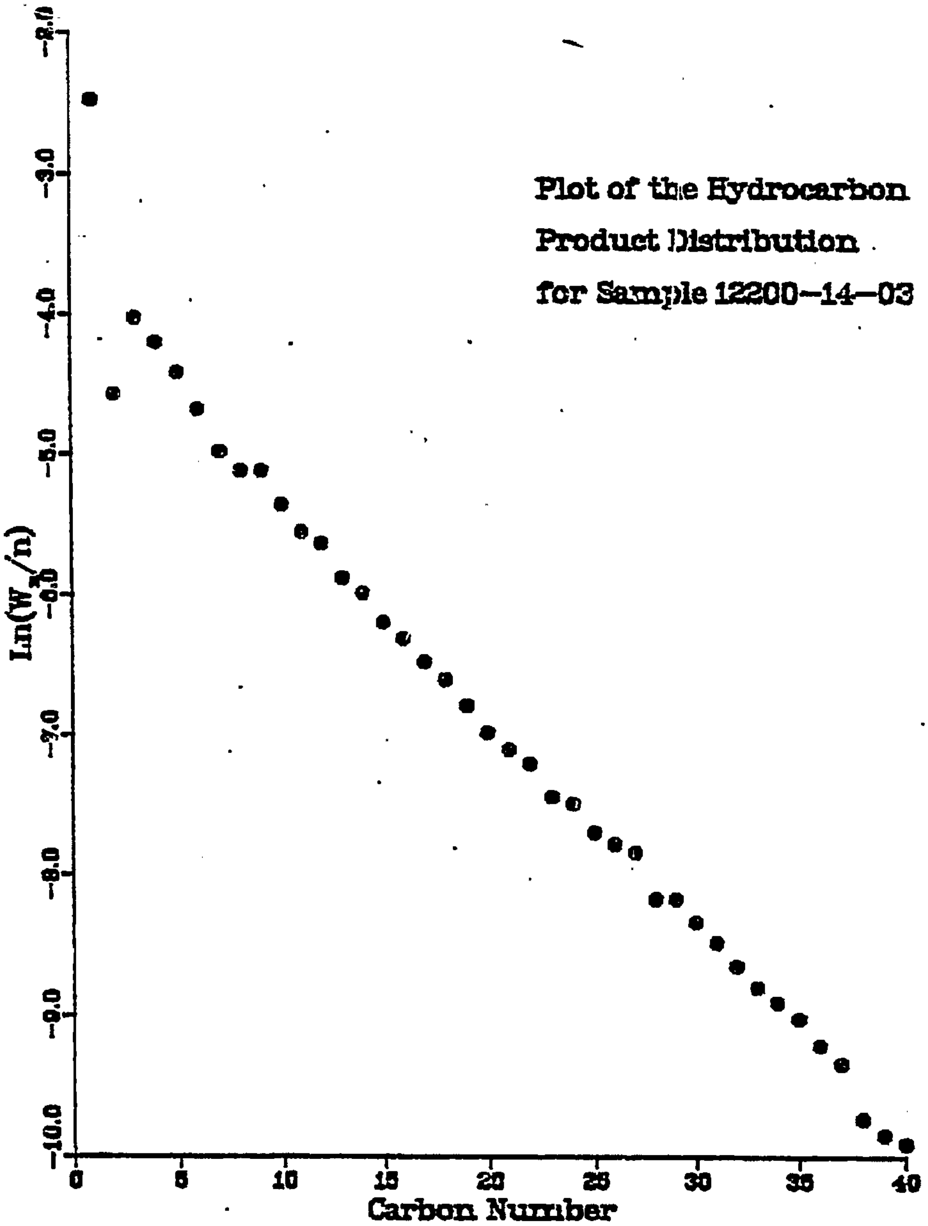
Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-01
Ln(W$_n$/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
Carbon Number

Fig. B344



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-02
Ln(W_n/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B345



Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-03
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
Ln(W$_n$/n)
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B346

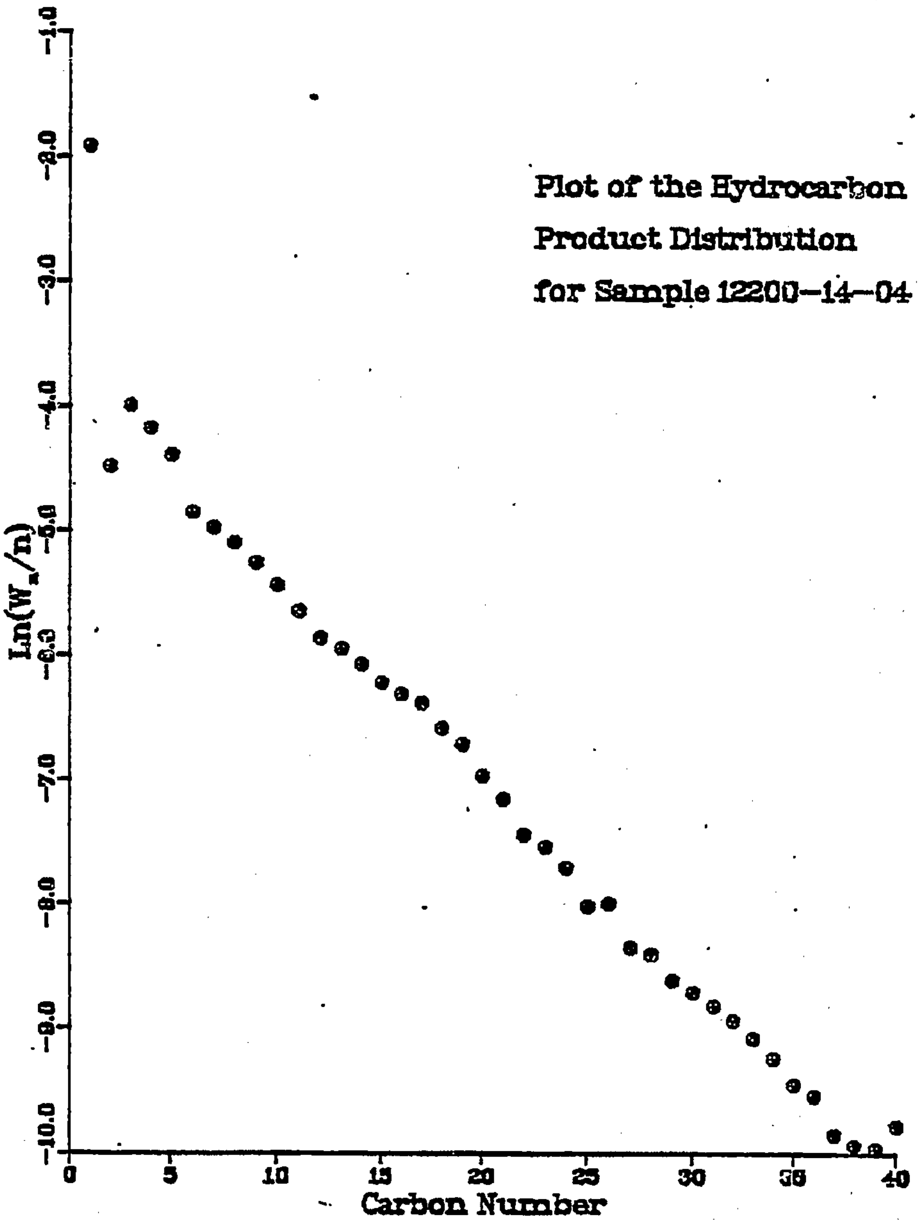

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-04
Ln(W_n/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B347

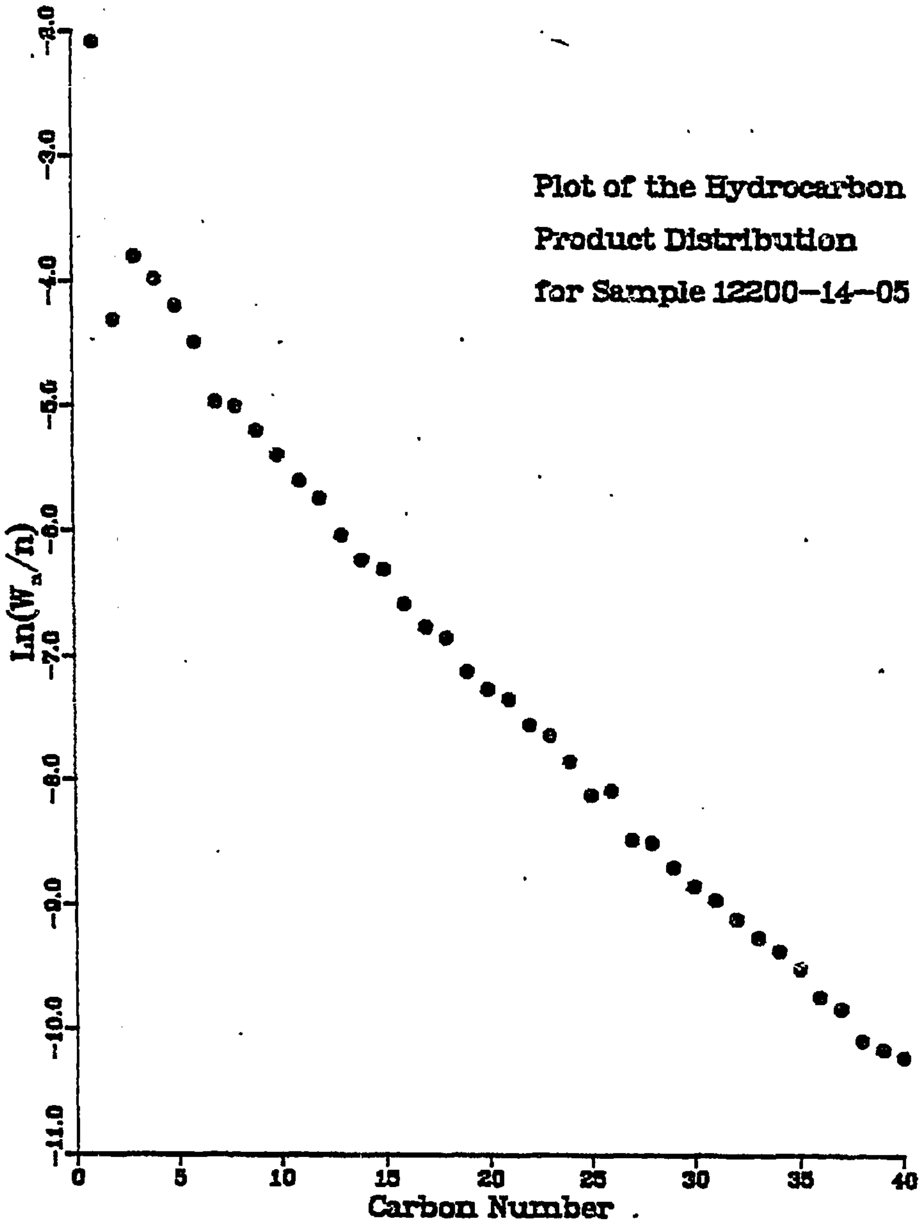

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-05
Ln(Wn/n)
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B348

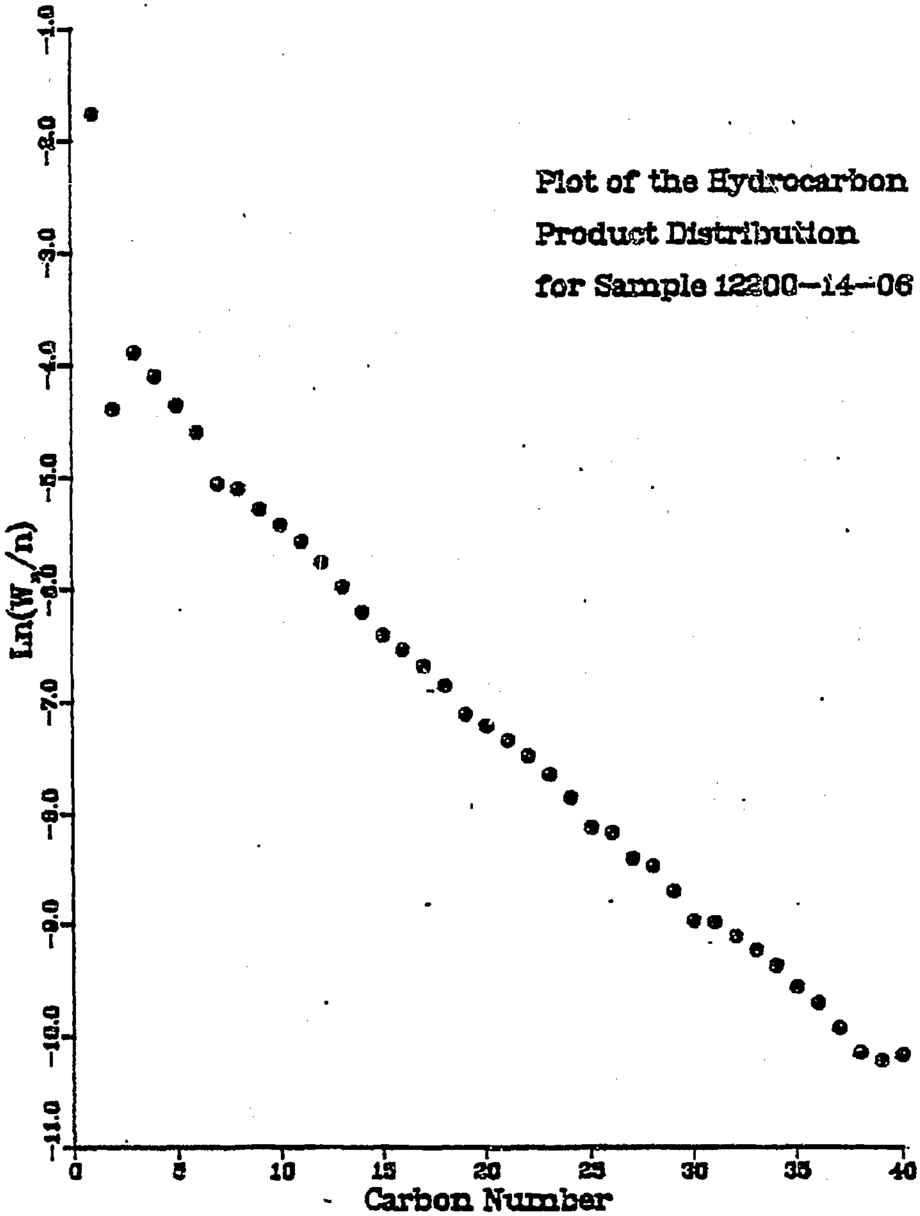
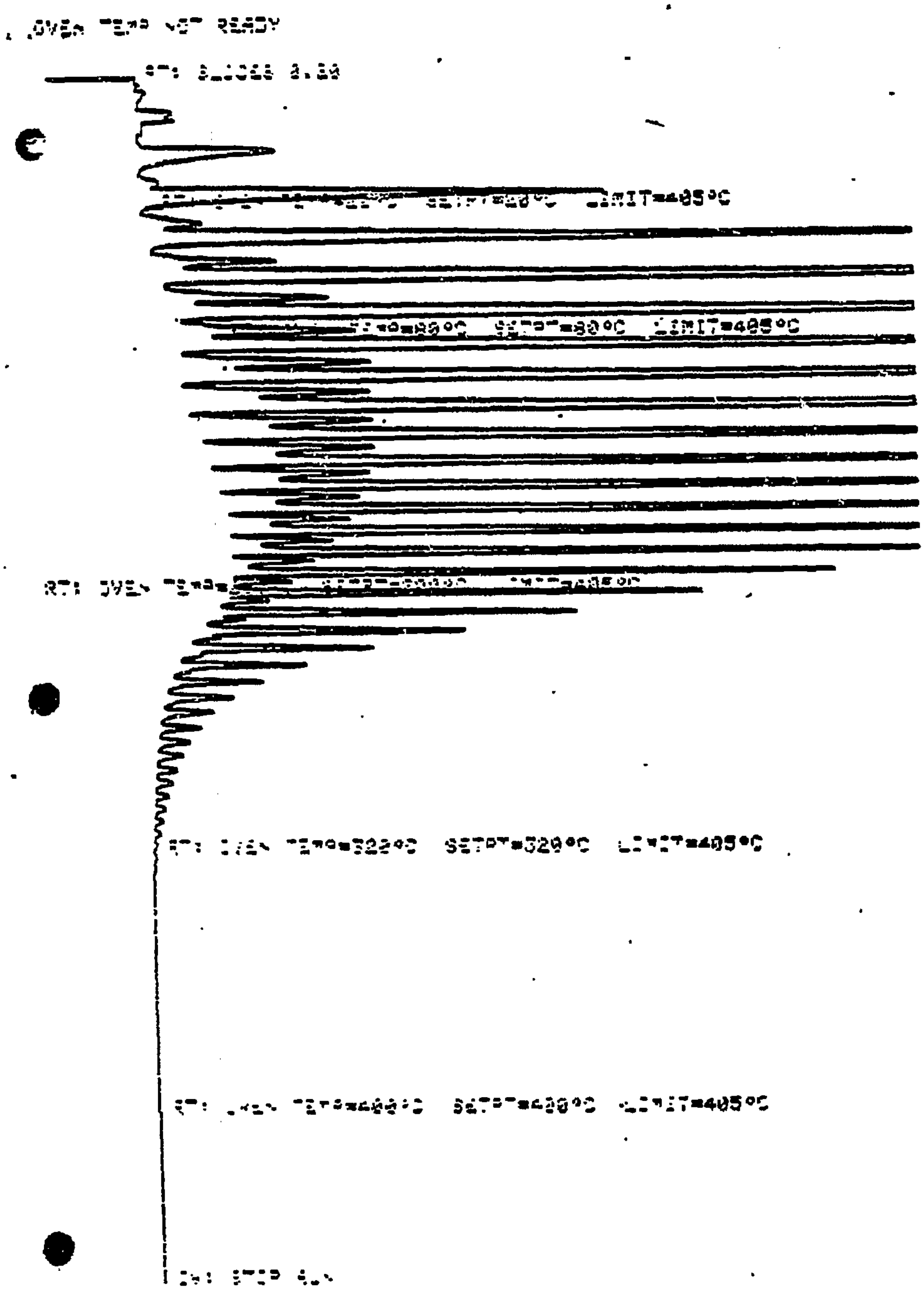
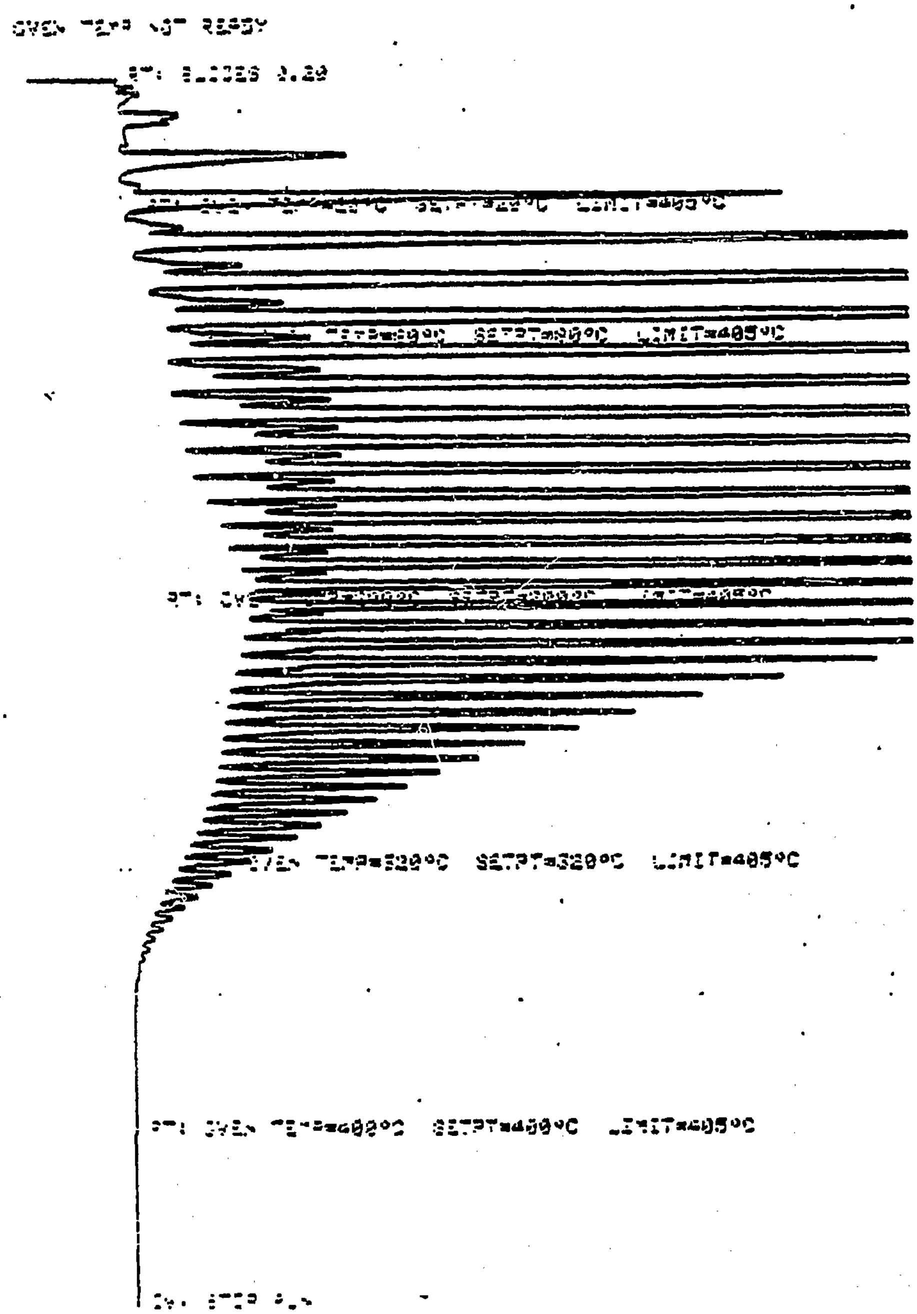

Plot of the Hydrocarbon
Product Distribution
for Sample 12200-14-06
Ln(W$_x$/n)
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
-8.0
-9.0
-10.0
-11.0
0
5
10
15
20
25
30
35
40
Carbon Number

Fig. B349



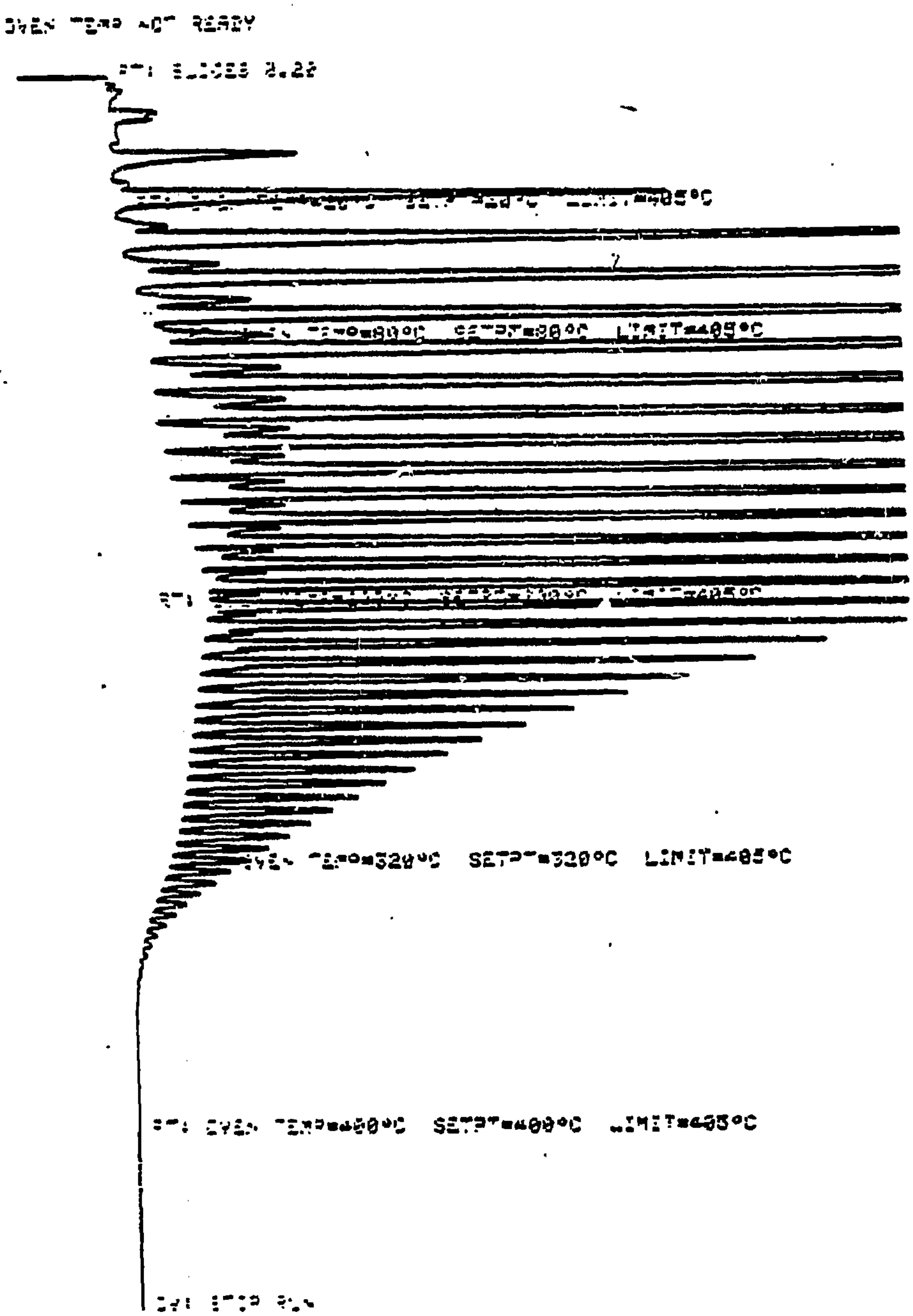
12200-14-01

Fig. B350



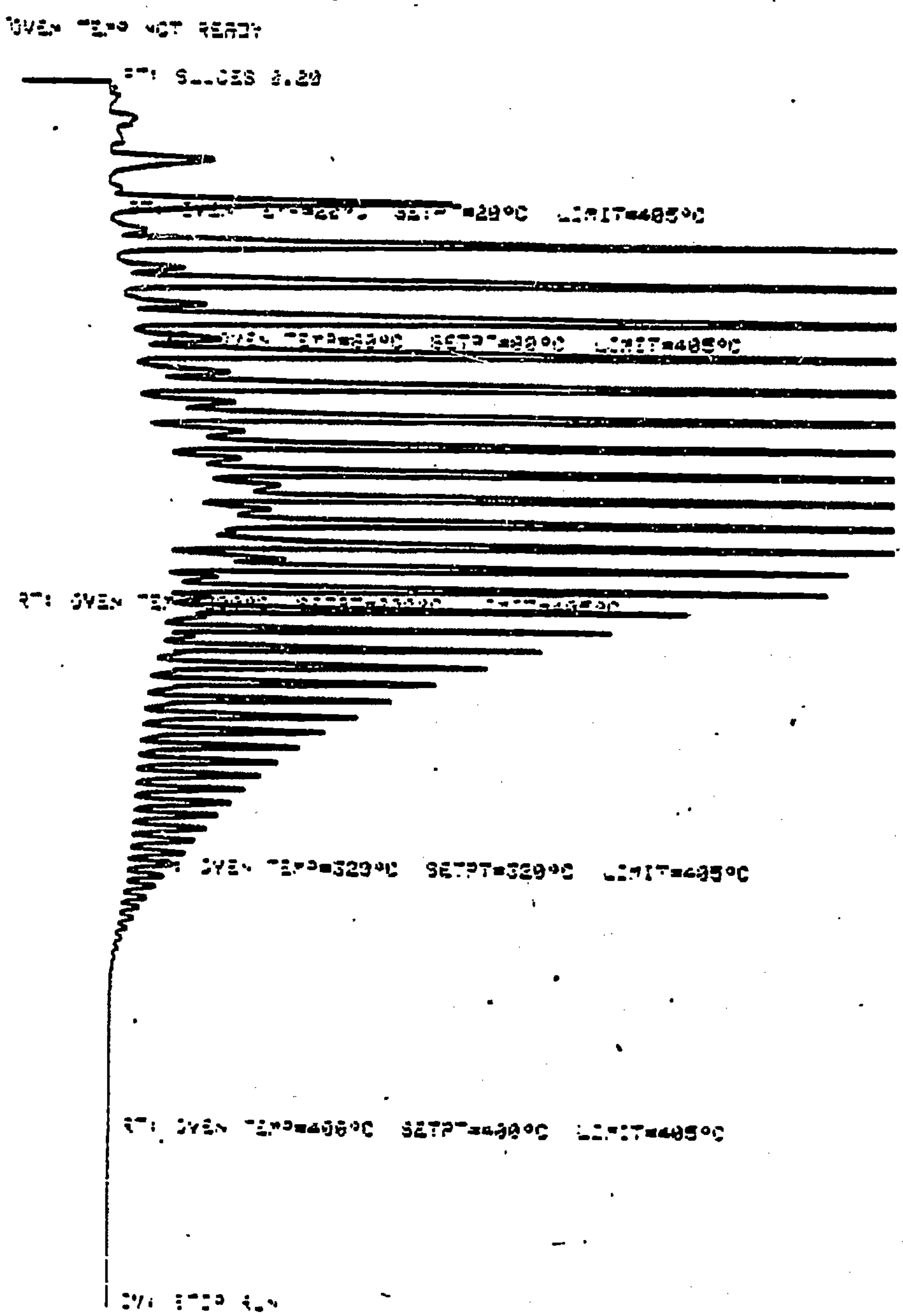
12200-14-02

Fig. B.51



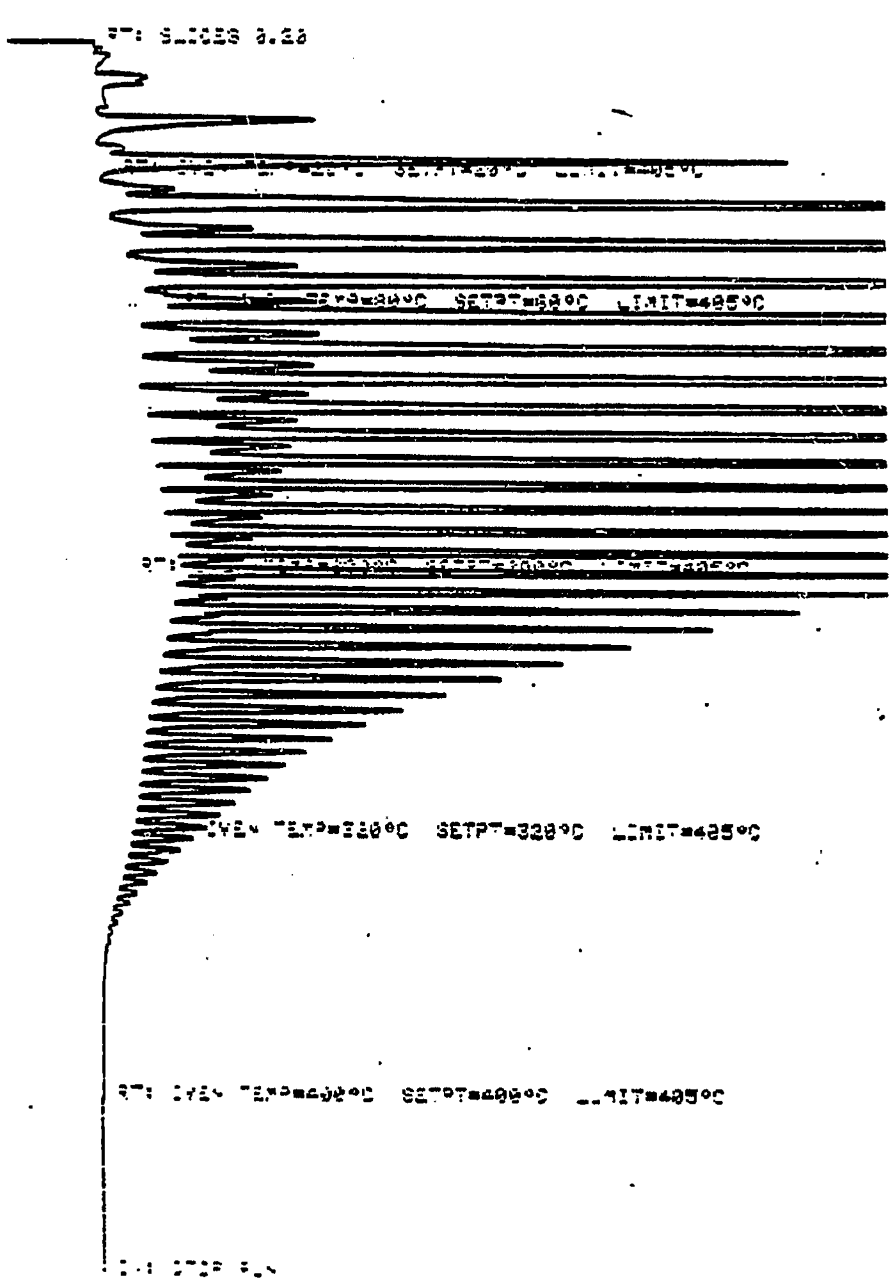
12200-14-3

Fig. B352



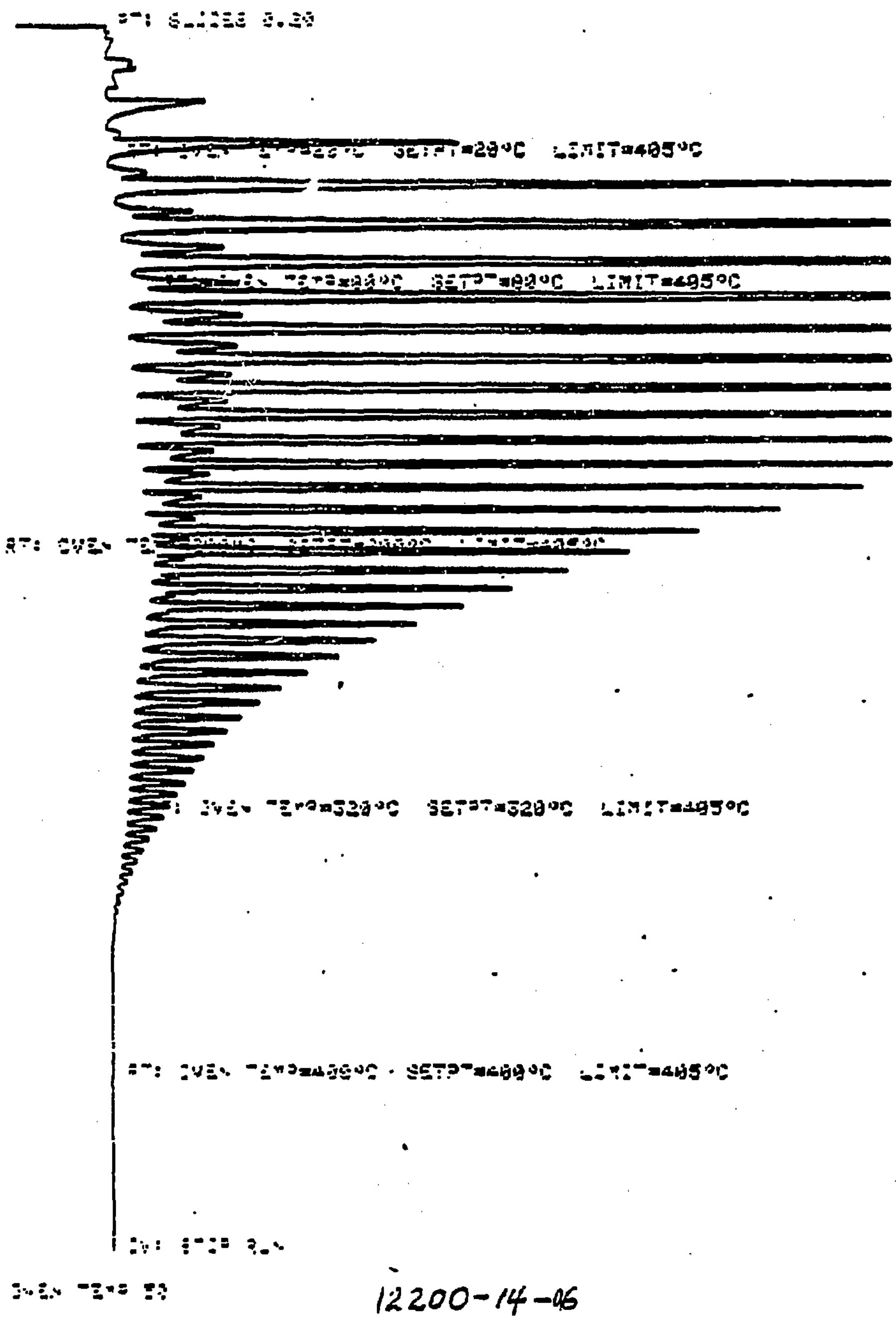
SAMPLE: 12200-14-04

Fig. B353



12200-14-05

Fig. B354



12200-14-06

Fig. B355

RESULT OF SYNGAS OPERATION

RUN NO. 12200-14
CATALYST CO/X10/X9/X4-U103 12251-41-21 80 CC 35.95 G (WT CHANGE +13.7G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-14-01	200-14-02	200-14-03	200-14-04	200-14-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	20.0	44.0	68.0	93.5	116.0
PRESSURE,PSIG	300	300	300	300	300
TEMP. C	264	259	259	259	259
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	20.00	24.00	24.00	25.50	22.50
EFFLNT GAS LITER	156.55	227.15	255.90	295.60	274.06
GM AQUEOUS LAYER	55.53	71.20	71.73	71.37	59.41
GM OIL	27.58	37.55	28.05	25.62	18.53
MATERIAL BALANCE					
GM ATOM CARBON %	82.17	88.50	88.07	90.83	91.08
GM ATOM HYDROGEN %	76.56	90.12	90.27	91.32	88.63
GM ATOM OXYGEN %	91.99	95.70	100.60	102.12	103.65
RATIO CHX/(H2O+CO2)	0.7617	0.8217	0.6925	0.7081	0.6628
RATIO X IN CHX	2.2433	2.3041	2.2891	2.4001	2.3719
USAGE H2/CO PRODT	1.6858	1.8871	2.0066	2.0210	2.0050
FEED H2/CO FRM EFFLNT	0.9316	1.0182	1.0250	1.0054	0.9731
RESIDUAL H2/CO RATIO	0.2118	0.3423	0.4171	0.4333	0.4566
RATIO CO2/(H2O+CO2)	0.2123	0.1372	0.1340	0.1386	0.1521
K SHIFT IN EFFLNT	0.0571	0.0544	0.0646	0.0697	0.0819
SPECIFIC ACTIVITY SA	6.7786	3.5637	2.2202	1.9321	1.6420
CONVERSION					
ON CO %	48.83	43.76	38.24	36.03	33.36
ON H2 %	88.37	81.09	74.87	72.43	68.73
ON CO+H2 %	67.90	62.59	56.78	54.28	50.81
PRDT SELECTIVITY,WT %					
CH4	6.45	9.72	8.43	14.73	12.46
C2 HC'S	1.76	1.60	2.07	2.27	2.69
C3H8	1.65	1.54	2.35	2.65	3.35
C3H6=	3.14	2.69	3.01	2.88	3.35
C4H10	1.62	1.54	2.20	2.35	3.01
C4H8=	3.95	3.32	3.82	3.79	4.46
C5H12	2.15	1.98	2.68	2.79	3.61
C5H10=	3.81	1.71	3.39	3.40	3.94
C6H14	2.60	2.30	3.05	2.79	3.99
C6H12= & CYCLO'S	2.40	0.00	2.14	1.40	2.38
C7+ IN GAS	8.11	7.00	8.27	9.44	9.89
LIQ HC'S	62.35	66.61	58.58	51.51	46.86
TOTAL	100.00	100.00	100.00	100.00	100.00

Table B26

SUB-GROUPING					
C1 -C4	18.57	20.40	21.89	28.67	29.32
C5 -420 F	45.89	35.96	39.74	36.92	41.86
420-700 F	32.11	29.84	25.89	25.14	20.48
700-END PT	3.43	13.79	12.48	9.27	8.34
C5+-END PT	81.43	79.60	78.11	71.33	70.68
ISO/NORMAL MOLE RATIO					
C4	0.0123	0.0137	0.0133	0.0000	0.0128
C5	0.0557	0.0458	0.0476	0.0000	0.0549
C6	0.0734	0.0620	0.0706	0.0000	0.0734
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.5022	0.5457	0.7451	0.8780	0.9520
C4	0.3954	0.4470	0.5566	0.5972	0.6498
C5	0.5495	1.1226	0.7670	0.7975	0.8906
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8177	0.8697	0.8512	0.8446	0.8292
RATIO CH4/(1-A)**2	1.9408	5.7227	3.8054	6.1001	4.2720
ALPHA FRM CORRELATION	0.8862	0.8631	0.8535	0.8516	0.8490
ALPHA (EXPTL/CORR)	0.9227	1.0077	0.9973	0.9918	0.9766
W%CH4 FRM CORRELATION	3.9544	10.0774	13.0651	13.6437	14.4332
W%CH4 (EXPTL/CORR)	1.6312	0.9642	0.6453	1.0797	0.8635
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX	OIL WAX	OIL WAX
DENSITY (* 40 C)	0.7456*	0.7694*	0.7751*	0.7706*	0.7636*
N, REFRACTIVE INDEX	1.4210*	1.4251*	1.4250*	1.4235*	1.4224*
SIMULT'D DISTILATN					
10 WT % @ DEG F	274	294	294	295	292
16	301	335	335	336	312
50	451	511	512	513	483
84	619	741	747	716	715
90	661	802	812	782	783
RANGE(16-84 %)	318	406	412	380	403
WT % @ 420 F	43.00	34.50	34.50	33.20	38.50
WT % @ 700 F	94.50	79.30	78.70	82.00	82.20

Table B26, cont

RESULT OF SYNGAS OPERATION

RUN NO. 12200-14
CATALYST CO/K10/X9/X4-U103 12251-41-21 80 CC 35.95 G (WT CHANGE +13.7G)
FEED H2:CO OF 50:50 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	12200-14-06
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	140.0
PRESSURE, PSIG	300
TEMP. C	259
FEED CC/MIN	400
HOURS FEEDING	24.00
EFFLNT GAS LITER	294.70
GM AQUEOUS LAYER	63.47
GM OIL	21.79
MATERIAL BALANCE	
GM ATOM CARBON %	91.09
GM ATOM HYDROGEN %	94.71
GM ATOM OXYGEN %	100.93
RATIO CHX/(H2O+CO2)	0.7348
RATIO X IN CHX	2.4501
USAGE H2/CO PRODT	1.9902
FEED H2/CO FRM EFFLNT	1.0398
RESIDUAL H2/CO RATIO	0.5076
RATIO CO2/(H2O+CO2)	0.1464
K SHIFT IN EFFLNT	0.0871
SPECIFIC ACTIVITY SA	1.5222
CONVERSION	
ON CO %	35.90
ON H2 %	68.70
ON CO+H2 %	52.62
PRDT SELECTIVITY, WT %	
CH4	17.11
C2 HC'S	2.47
C3H8	3.12
C3H6=	2.99
C4H10	2.74
C4H8=	3.91
C5H12	3.29
C5H10=	3.12
C6H14	3.59
C6H12= & CYCLO'S	2.08
C7+ IN GAS	9.01
LIQ HC'S	46.57
TOTAL	100.00

Table B27

SUB-GROUPING	
C1 -C4	32.34
C5 -420 F	38.78
420-700 F	20.72
700-END PT	8.15
C5+-END PT	67.66
ISO/NORMAL MOLE RATIO	
C4	0.0142
C5	0.0583
C6	0.0768
C4=	0.0000
PARAFFIN/OLEFIN RATIO	
C3	0.9947
C4	0.6760
C5	1.0245
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8337
RATIO CH4/(1-A)**2	6.1891
ALPHA FRM CORRELATION	0.8439
ALPHA (EXPTL/CORR)	0.9880
W%CH4 FRM CORRELATION	16.0351
W%CH4 (EXPTL/CORR)	1.0671
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL WAX
DENSITY (* 40 C)	0.7637*
N, REFRACTIVE INDEX	1.4226*
SIMULT'D DISTILATN	
10 WT % @ DEG F	293
16	331
50	483
84	711
90	781
RANGE(16-84 %)	380
WT % @ 420 F	38.00
WT % @ 700 F	82.50

Table B27, cont

XVII. Summary

The work reported in this Quarter has been fruitful both in establishing the means for obtaining some of the essential properties of a fully effective catalyst, and in developing promising lines for future investigation.

Significant improvements have been obtained on the intimately contacted cobalt/UCC-103 catalyst system developed during the previous contract.

A new method has been tested for preparing cobalt in intimate contact with a Molecular Sieve, which shows considerable promise for improving both activity and product selectivity.

In the catalysts prepared by the previous method of formulation, thoria was successfully replaced by a combination of additives X_9 and X_{10}.

The combination of these additives with X_4 has produced a catalyst with excellent stability, some reduction of methane, and a higher specific activity than the most stable catalyst yet developed (Catalyst 6, Run 11677-11, Third Annual Report of the previous contract). The product was lower in olefinic content, but results with Catalysts 21 and 23 suggest that this might be corrected with a higher concentration of X_4.

Attempts to raise the specific activity of these catalysts above 2.0 were unsuccessful. Incorporation of a second shape-

selective component (UCC-101, UCC-112), was found to contribute little or nothing to product quality. An attempt to replicate the results of Catalyst 11677-11 failed, probably due to a lower ratio of thorium to cobalt than in the original.

A new method of intimately combining cobalt oxide with UCC-103, first tested in Catalyst 11, resulted in unprecedented high initial specific activity of 12.5 and water gas shift activity of 69 percent oxygen conversion to CO_2, but very poor stability. Similar results were obtained with Catalyst 24, in which UCC-113 was substituted for UCC-103. Several attempts to improve stability, including the use of additives X_9, X_{10} and X_4, were unsuccessful.

Iron was tested as the Fischer-Tropsch metal component in Catalysts 17 and 18. Both proved low in activity, although Catalyst 17 did produce a much lower methane yield and a substantially higher olefin content of the C_4's.

An unexpected result with Catalyst 20, which warrants further investigation, was the appearance of a possible carbon number cutoff.

The most significant opportunity for future work, however, lies in improving the stability of catalysts incorporating the new method of combining cobalt with UCC-103, UCC-113 or other shape-selective components.

Appendix C. COMPARISON BETWEEN UCC AND GULF-BADGER PROCESS OF FISCHER-TROPSCH SYNTHESIS FOR DIESEL PRODUCTION

Appendix C. COMPARISON BETWEEN UCC AND GULF-BADGER PROCESS OF FISCHER-TROPSCH SYNTHESIS FOR DIESEL PRODUCTION

C-L Yang and A. C. Frost

Gulf-Badger has reported a process for converting natural gas to hydrocarbon liquid fuel via steam reforming and Fischer-Tropsch synthesis (A. H. Singleton and S. Regier, Hydrocarbon Processing, May 1983).

Since Gulf-Badger's Fischer-Tropsch synthesis process/catalyst system appears to be similar to that proposed by Union Carbide Corporation (UCC) for the MITRE economic study, the Department of Energy requested that we compare the two systems.

Such comparisons have accordingly been made of (1) the product distribution from the Gulf-Badger fixed bed pilot plant (Table 2, Page 73 of the article), (2) the temperature versus syngas conversions for the Gulf-Badger fixed bed pilot plant (Figure 5, Page 73 of the article), and (3) the liquid product distribution from the Gulf-Badger demonstration plant (fourth paragraph from the end of the article, page 74).

The findings of these comparisons indicate (with many assumptions) that the Gulf-Badger system may operate at a 40-50C lower temperature and at an ill-defined higher H_2:CO ratio than does the UCC system to give a product distribution having slightly more naphtha but less distillate and wax.

These findings are detailed for the following aforementioned areas.

1. Pilot Plant Product Distribution

The product distribution given for the Gulf-Badger pilot plant (Table 2, page 73 of the article) is repeated in Column 2 of Table C1 of this Appendix. This distribution has the same general type of selectivity that has been found for the UCC Fischer-Tropsch catalyst, i.e., a relatively high methane make and a liquid product containing a considerable amount of distillate plus material.

Column 3 presents the product distribution normalized to an oxygen-species free basis, a form useful in calculating the Column 4 Schulz-Flory alpha's for each of the product cuts quantified by Column 3 and defined by Column 1.

It can be seen that these Column 4 alpha's hop around a bit over a range from a low of 0.800 to a high of 0.855. This fact, plus the additional fact that Figure 4 on page 73 of the reference shows three liquid products having boiling ranges which more closely correspond to C_5-C_9 for the naphtha and C_{10}-C_{20} for distillate, prompted the Column 5 recalculation of Schulz-Flory alpha's based on these new definitions for the cuts quantified in Column 3.

The far smaller scatter in these recalculated Column 5 alpha's indicates the possibility that the descriptions of the product cuts given in Table 2 of the reference may be better defined in the manner described above.

2. Temperature versus Conversion

The temperature versus syngas conversion plot given for the Gulf-Badger pilot plant (Figure 5, page 73 of the article) for different H_2:CO feed ratios is reshown as Figure C1 of this Appendix. Also shown in Figure C1 are similar computer plots from the UCC catalyst used in the same type of tubular reactor operating with no recycle stream.

Although the UCC computer simulation employed the same 715 GHSV used by Gulf-Badger, the operating pressure was set at 300 psig, rather than the 250 psig used by Gulf-Badger, since this was the only pressure at which the rate expressions for UCC's catalyst have yet been correlated.

Figure C1 shows that the plotted curves for the UCC catalyst not only include those for the same 2.0, 1.7, and 1.5 H_2:CO feed ratios given by Gulf-Badger, but also include additional curves for 1.0, 0.8, 0.7, and 0.65 H_2:CO feed ratios as well.

These additional curves for the lower H_2:CO ratios were included because it is only at these lower feed ratios that the UCC catalyst can produce a product having a high C_5^+ yield. This is seen from the product distributions given in Table C2. These distributions show that only at H_2:CO feed ratios of 0.7 or lower are the C_5^+ yields above an acceptable 70 percent at the 10-55 percent syngas conversions shown in Figure C1 for the Gulf-Badger catalyst.

These results indicate that <u>if</u> the Gulf-Badger catalyst produces the product distribution shown in their Table 2 <u>at</u> the conditions indicated by their Figure 5, the UCC catalyst must be run at a 40-50C higher temperature and a 50-70 percent lower H_2:CO ratio to achieve the same sort of conversions and product distributions achieved by the Gulf-Badger catalyst.

3. Demonstration Plant Product Distribution

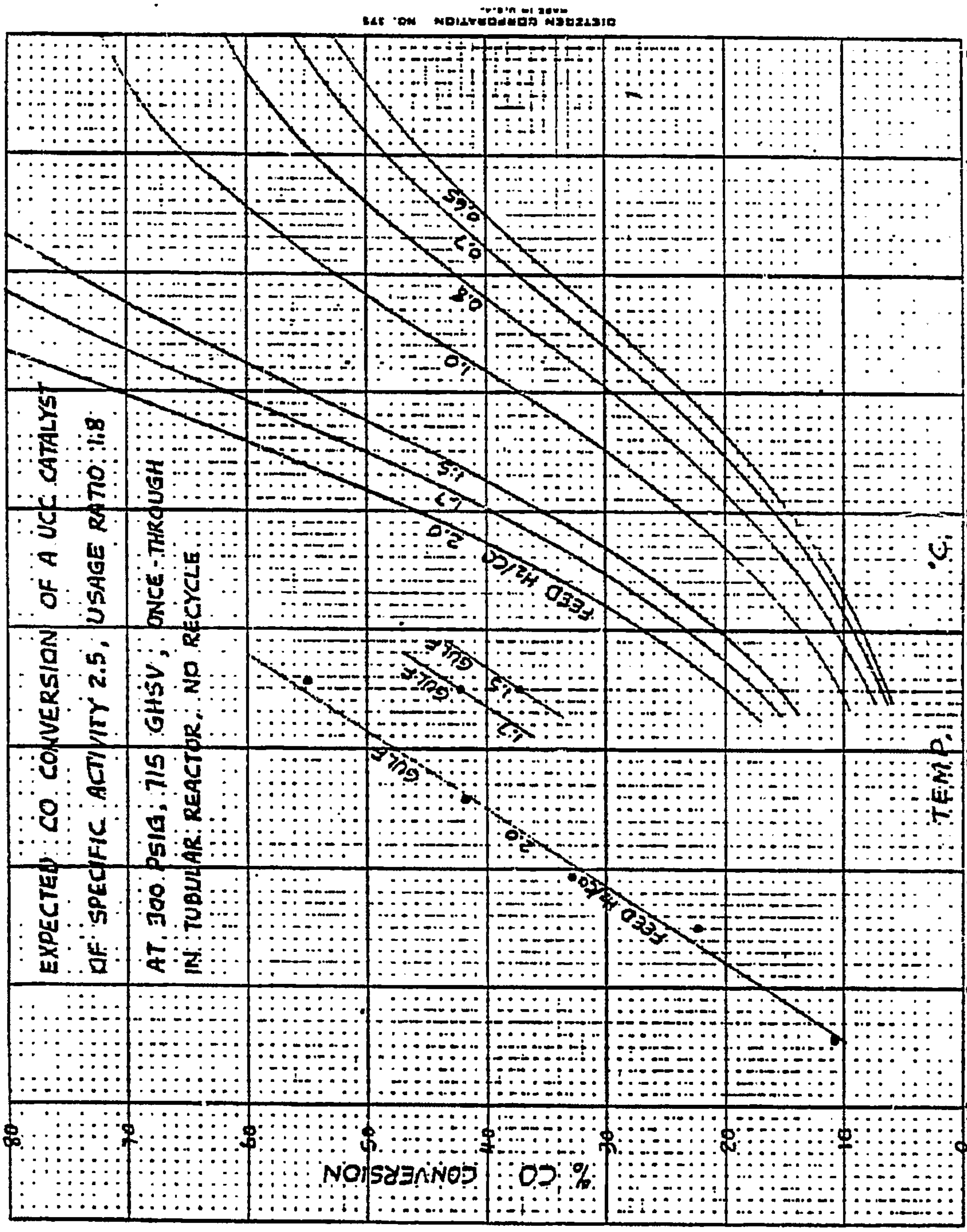
The Gulf-Badger demonstration plant is shown in Figure 8 of their article as employing a recycle stream, a configuration that is common with our own process. Consequently, the product distribution from this Gulf-Badger process configuration can be expected to be comparable to those of our own.

The product distribution for the Gulf-Badger demonstration plant was described on page 74 of their article as approximately 15 bpd of naphtha, 15 bpd of diesel fuel, and 7 bpd of wax. Table C3 compares these values with those from a UCC catalyst (S.A.=2.5, U=1.8, S.G.=0.6) operating in a tubular reactor at 300 psig, 270C, and a 2.3 recycle ratio (only the non-condensibles from the reactor effluent are recycled) with a 1.35 H_2:CO feed ratio required to give a 13.94 weight percent CH_4 make (arbitrarily chosen to match the oxygen-free pilot plant value given in Table 2 of their article) and with a 379 GHSV required to ensure an overall 85 percent syngas conversion.

The UCC product distributions so obtained under these conditions are shown in Table C3 on a consistent total 37 bpd basis for naphtha defined both as C_5-C_8 and as C_5-C_9, the two possible definitions for naphtha discussed in the first section of this report.

Table C4 shows the same type of comparison with product from the same UCC catalyst (S.A.=2.5, U=1.8, S.G.=0.6) in a tubular reactor operating at the same 270F, 300 psig, 2.3 recycle ratio, but employing a 1.30 H_2:CO feed ratio required to give a more economically desirable 10.0 weight percent CH_4 make (instead of the 13.9 weight percent make for the Table C3 case) and now using a 265 GHSV (instead of the 379 GHSV for the Table C3 case) to achieve the 85 percent overall syngas conversion.

The Table C3 results show that when the UCC catalyst/process system is operated at conditions giving a 13.9 percent CH_4 make, it produces 24-38 volume percent less gasoline, 9-23 volume percent more diesel, and 30 volume percent more wax than does the Gulf-Badger system. Similarly, the Table C4 results show that when the UCC catalyst/process system is operated at conditions giving an economically more desirable 10.0 weight percent CH_4 make, it produces 14-29 volume percent less gasoline, 11-27 volume percent more diesel, and 6 volume percent more wax than does the Gulf-Badger system.


EXPECTED CO CONVERSION OF A UCC CATALYST
OF SPECIFIC ACTIVITY 2.5, USAGE RATIO 1.8
AT 300 PSIG, 715 GHSV, ONCE-THROUGH
IN TUBULAR REACTOR, NO RECYCLE
FEED H2/CO
% CO CONVERSION
TEMP. °C

[Fig. C1]

Table C1. Analysis of Gulf-Badger's pilot plant product distribution.

(1) Product components	(2) Table 2 reference listing	(3) Table 2 reference listing, oxygen free basis	(4) Schulz-Flory alpha's for each product cut quantified in col. 3 and defined by col. 1	(5) Schulz-Flory alpha's for each product cut quantified in col. 3 and defined as C_5-C_9 being naphtha & C_{10}-C_{20} being distillate
CH_4	13.7	13.937	—	—
C_2H_4 to C_4H_{10}	11.6	11.801	0.855	0.855
C_5-C_8 naphtha	25.4	25.839	0.811	0.849
C_9-C_{20} distillate	33.4	33.978	0.800	0.846
C_{21}&+ wax	14.2	14.445	0.853	0.853
Oxygenate	1.7			
Total	100.0	100.000		

Table C2. Simulated conversions and product distributions at different temperatures and H_2:CO feed ratios for a UCC catalyst in a tubular reactor having no recycle. Feed space velocity: 715. Reactor pressure: 300 psig. UCC catalyst: S.A.=2.5, U=1.8, ρ=0.6 gm/cc.

	Temperature, deg C						
	215	220	230	240	250	260	270
Feed gas H_2:CO ratio: 2.00							
Conv H_2	19.267	25.832	44.180	68.216	89.119		
Conv CO	21.407	28.702	49.087	75.795	99.020		
Conv SG	19.980	26.788	45.814	70.742	92.418		
Average alpha	0.77915	0.77858	0.77706	0.77447	0.76959		
FCH_4*	5.32866	5.59073	6.09518	6.57620	7.13748		
CH_4	25.990	27.411	30.294	33.448	37.892		
C_2–C_4	20.006	19.699	19.114	18.580	18.035		
C_5–C_8	24.767	24.328	23.452	22.533	21.245		
C_9–C_{20}	26.372	25.787	24.560	23.109	20.859		
C_{21}&+	2.865	2.776	2.580	2.330	1.969		
C_5^+	54.004	52.890	50.592	47.972	44.073		
Feed gas H_2:CO ratio: 1.70							
Conv H_2	17.663	23.685	40.587	63.225	84.599	95.577	98.748
Conv CO	16.681	22.369	38.332	59.712	79.899	90.267	93.262
Conv SG	17.298	23.197	39.751	61.923	82.858	93.610	96.716
Average alpha	0.78792	0.78770	0.78744	0.78760	0.78858	0.79051	0.79255
FCH_4*	5.17338	5.45327	5.99117	6.50326	7.00008	7.51567	8.08147
CH_4	23.268	24.578	27.070	29.340	31.290	32.983	34.778
C_2–C_4	19.496	19.194	18.595	17.997	17.384	16.758	16.171
C_5–C_8	25.052	24.640	23.845	23.092	22.388	21.709	21.008
C_9–C_{20}	28.603	28.084	27.120	26.295	25.684	25.236	24.654
C_{21}&+	3.582	3.504	3.370	3.276	3.254	3.314	3.388
C_5^+	57.236	56.228	54.335	52.663	51.326	50.259	40.050

*The ratio of the amount of CH_4 actually produced to the amount of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.

continued

Table C2, continued.

	Temperature, deg C						
	215	220	230	240	250	260	270
Feed gas H_2:CO ratio: 1.50							
Conv H_2	16.465	22.061	37.747	58.909	79.919	92.611	97.435
Conv CO	13.721	18.384	31.456	49.090	66.599	77.176	81.196
Conv SG	15.366	20.589	35.230	54.981	74.590	86.436	90.938
Average alpha	0.79449	0.79445	0.79478	0.79606	0.79897	0.80346	0.80795
FCH_4*	5.02734	5.32229	5.88812	6.42860	6.97041	7.58658	8.32411
CH_4	21.233	22.487	24.797	26.737	28.171	29.304	30.701
C_2–C_4	19.065	18.767	18.163	17.530	16.838	16.110	15.455
C_5–C_8	25.184	24.786	24.021	23.300	22.615	21.906	21.148
C_9–C_{20}	30.299	29.811	28.965	28.376	28.144	28.078	27.680
C_{21}&+	4.220	4.149	4.054	4.057	4.232	4.601	5.016
C_5^+	59.702	58.747	57.040	55.733	54.991	54.586	53.844
Feed gas H_2:CO ratio: 1.00							
Conv H_2	13.137	17.597	30.173	47.725	67.470	83.553	92.739
Conv CO	7.299	9.777	16.763	26.515	37.484	46.419	51.522
Conv SG	10.217	13.686	23.466	37.119	52.476	64.985	72.129
Average alpha	0.81501	0.81525	0.81641	0.81897	0.82357	0.83015	0.83713
FCH_4*	4.34412	4.69799	5.36936	6.00100	6.62691	7.33555	8.23159
CH_4	14.867	16.036	18.098	19.667	20.629	21.163	21.834
C_2–C_4	17.461	17.186	16.601	15.936	15.158	14.297	13.500
C_5–C_8	25.116	24.744	24.010	23.271	22.487	21.602	20.650
C_9–C_{20}	35.628	35.168	34.437	34.046	34.044	34.185	33.905
C_{21}&+	6.928	6.866	6.856	7.080	7.682	8.753	10.110
C_5^+	67.673	66.778	65.302	64.397	64.213	64.540	64.666

*The ratio of the amount of CH_4 actually produced to the amount of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.

continued

Table C2, continued.

	Temperature, deg C						
	215	220	230	240	250	260	270
Feed gas H_2:CO ratio: 0.80							
Conv H_2	11.596	15.545	26.740	42.660	61.461	78.390	89.522
Conv CO	5.154	6.910	11.885	18.961	27.317	34.841	39.788
Conv SG	8.016	10.746	18.486	29.493	42.491	54.195	61.891
Average alpha	0.82602	0.82630	0.82756	0.83020	0.83481	0.84139	0.84866
FCH_4*	3.78335	4.17899	4.92348	5.61216	6.27350	6.98716	7.87882
CH_4	11.452	12.609	14.641	16.180	17.119	17.577	18.045
C_2–C_4	16.456	16.199	15.641	14.993	14.221	13.347	12.507
C_5–C_8	24.758	24.399	23.673	22.916	22.081	21.119	20.071
C_9–C_{20}	38.388	37.916	37.157	36.718	36.622	36.646	36.274
C_{21}&+	8.946	8.878	8.888	9.193	9.958	11.311	13.103
C_5^+	72.092	71.192	69.718	68.827	68.661	69.076	69.449
Feed gas H_2:CO ratio: 0.70							
Conv H_2	10.757	14.427	24.876	39.893	58.074	75.263	87.389
Conv CO	4.184	5.612	9.675	15.515	22.585	29.270	33.986
Conv SG	6.889	9.240	15.933	25.552	37.198	48.207	55.974
Average alpha	0.83255	0.83283	0.83409	0.83670	0.84120	0.84765	0.85493
FCH_4*	3.36195	3.78689	4.58244	5.31023	5.99451	6.70788	7.58787
CH_4	9.427	10.583	12.614	14.160	15.116	15.569	15.970
C_2–C_4	15.816	15.572	15.036	14.404	13.646	12.778	11.922
C_5–C_8	24.434	24.083	23.366	22.602	21.743	20.745	19.647
C_9–C_{20}	39.948	39.464	38.673	38.180	37.996	37.912	37.442
C_{21}&+	10.375	10.299	10.312	10.654	11.500	12.997	15.020
C_5^+	74.757	73.845	72.351	71.435	71.239	71.654	72.109

*The ratio of the amount of CH_4 actually produced to the amount of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.

continued

Table C2, continued.

	Temperature, deg C						
	215	220	230	240	250	260	270
Feed gas H_2:CO ratio: 0.65							
Conv H_2	10.315	13.840	23.896	38.432	56.257	73.525	86.144
Conv CO	3.725	4.999	8.630	13.880	20.316	26.552	31.109
Conv SG	6.320	8.481	14.643	23.551	34.474	45.055	52.788
Average alpha	0.83616	0.83644	0.83769	0.84026	0.84468	0.85102	0.85827
FCH_4*	3.09461	3.53747	4.36423	5.11582	5.81391	6.52637	7.40010
CH_4	8.307	9.464	11.498	13.054	14.025	14.484	14.866
C_2-C_4	15.450	15.213	14.690	14.070	13.321	12.460	11.599
C_5-C_8	24.218	23.873	23.161	22.395	21.526	20.511	19.387
C_9-C_{20}	40.776	40.284	39.473	38.944	38.704	38.551	38.014
C_{21}&+	11.248	11.167	11.179	11.537	12.423	13.994	16.134
C_5^+	76.242	75.323	73.812	72.876	72.654	73.056	73.536

*The ratio of the amount of CH_4 actually produced to the amount of CH_4 predicted from the Schulz-Flory equation, $[CH_4/(1-\alpha)^2]$.

Table C3. Comparison of product distributions with the UCC system producing 13.94 weight percent CH_4 and for naphtha defined in two ways.

	Union Carbide, 14 wt pct CH_4		Gulf-Badger demonstration unit	
	Yield, barrels per day	Individual alpha	Yield, barrels per day	Individual alpha
Naphtha defined as C_5-C_8				
Naphtha	10.58	0.859	15.0	0.792
Diesel	19.03	0.872	15.0	0.782
Wax	7.39	0.859	7.0	0.857
Total	37.00		37.0	
Naphtha defined as C_5-C_9				
Naphtha	12.94	0.858	15.0	0.836
Diesel	16.66	0.859	15.0	0.818
Wax	7.40	0.859	7.0	0.856
Total	37.00		37.0	

Table C4. Comparison of product distributions with the UCC system producing 10 weight percent CH_4 and for naphtha defined in two ways.

	Union Carbide, 10 wt pct CH_4		Gulf-Badger demonstration unit	
	Yield, barrels per day	Individual alpha	Yield, barrels per day	Individual alpha
Naphtha defined as C_5-C_8				
Naphtha	9.30	0.872	15.0	0.792
Diesel	18.51	0.879	15.0	0.782
Wax	9.19	0.873	7.0	0.857
Total	37.00		37.0	
Naphtha defined as C_5-C_9				
Naphtha	11.44	0.872	15.0	0.836
Diesel	16.36	0.882	15.0	0.818
Wax	9.20	0.873	7.0	0.856
Total	37.00		37.0	

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