

Fig. 73

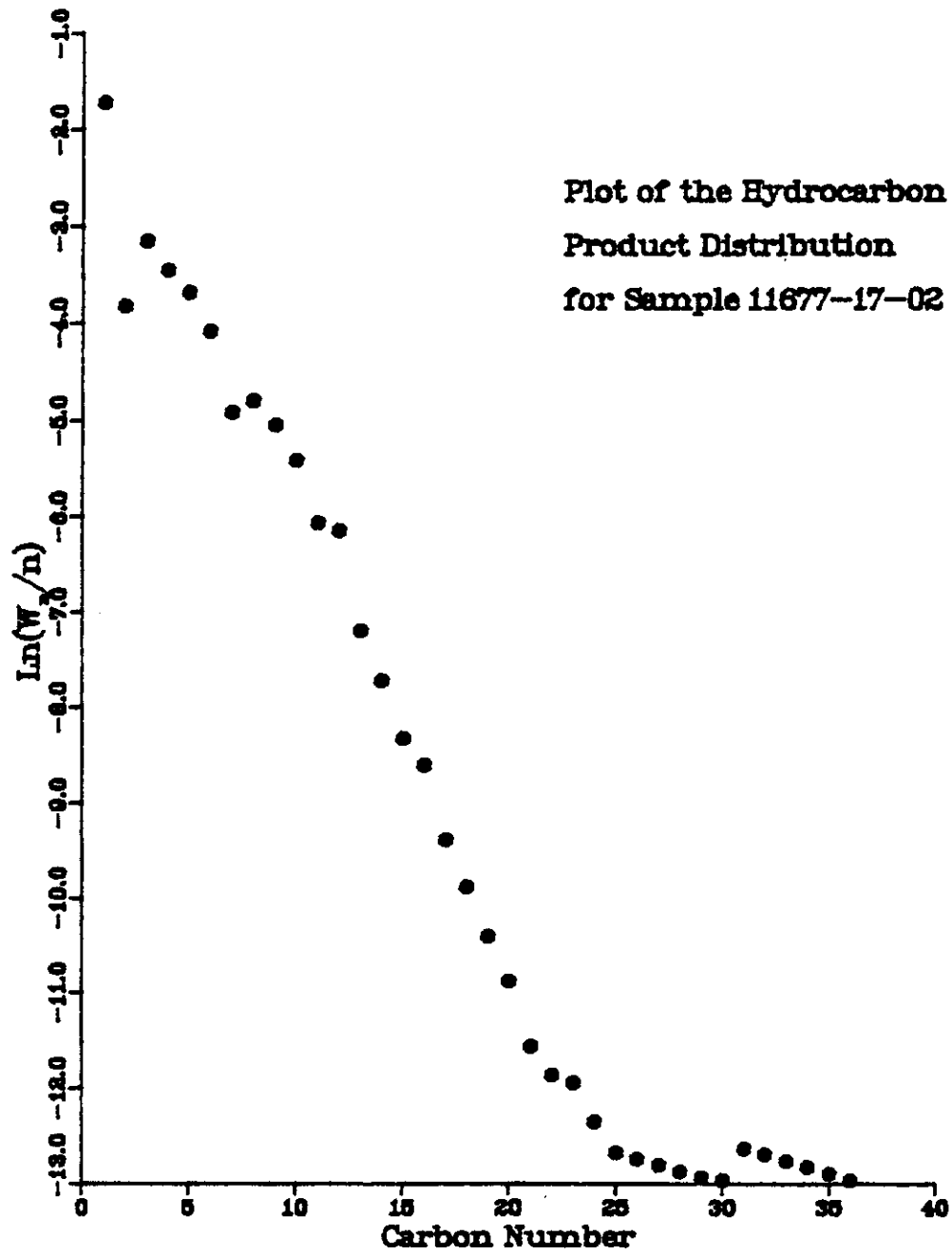


Fig. 74

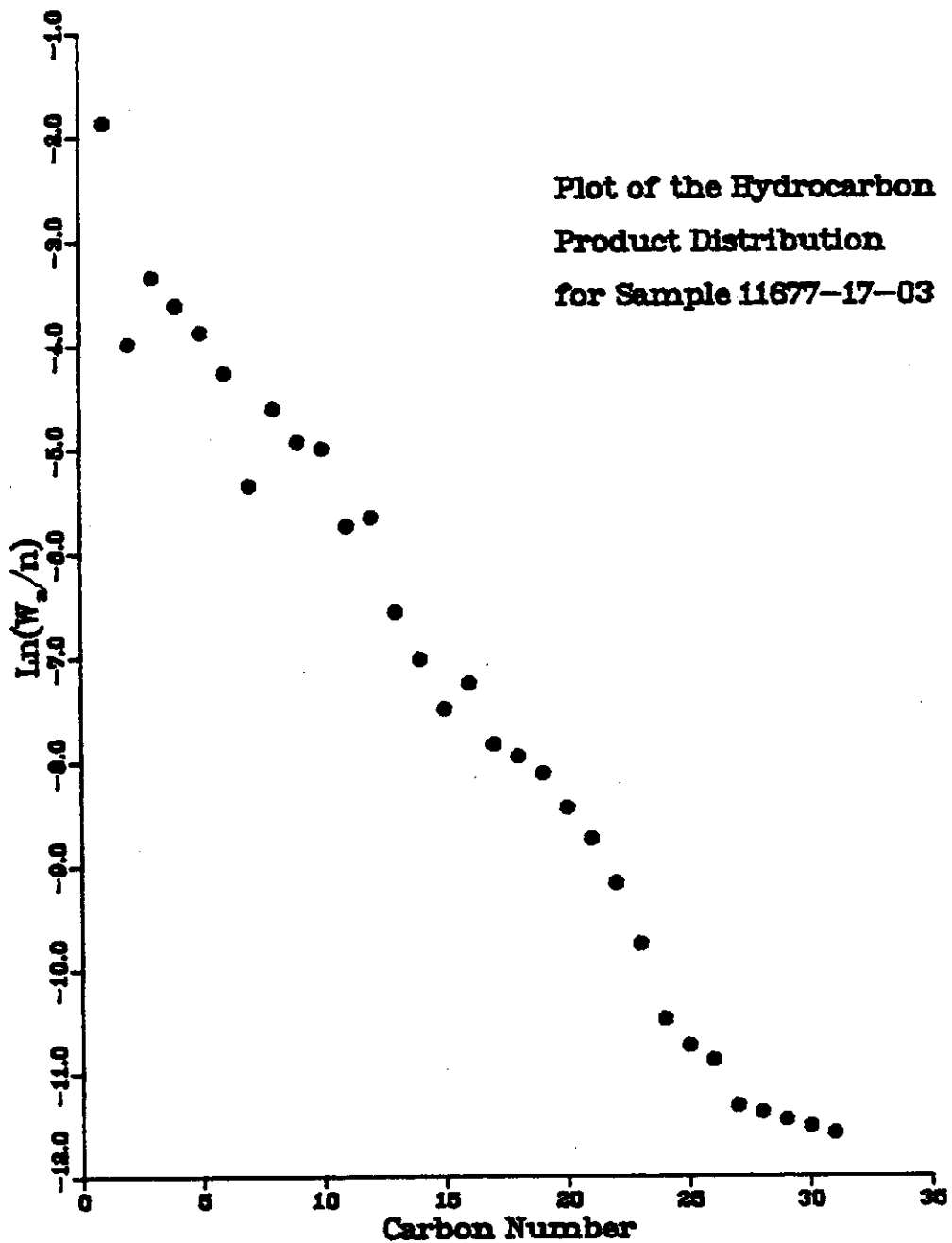


Fig. 75

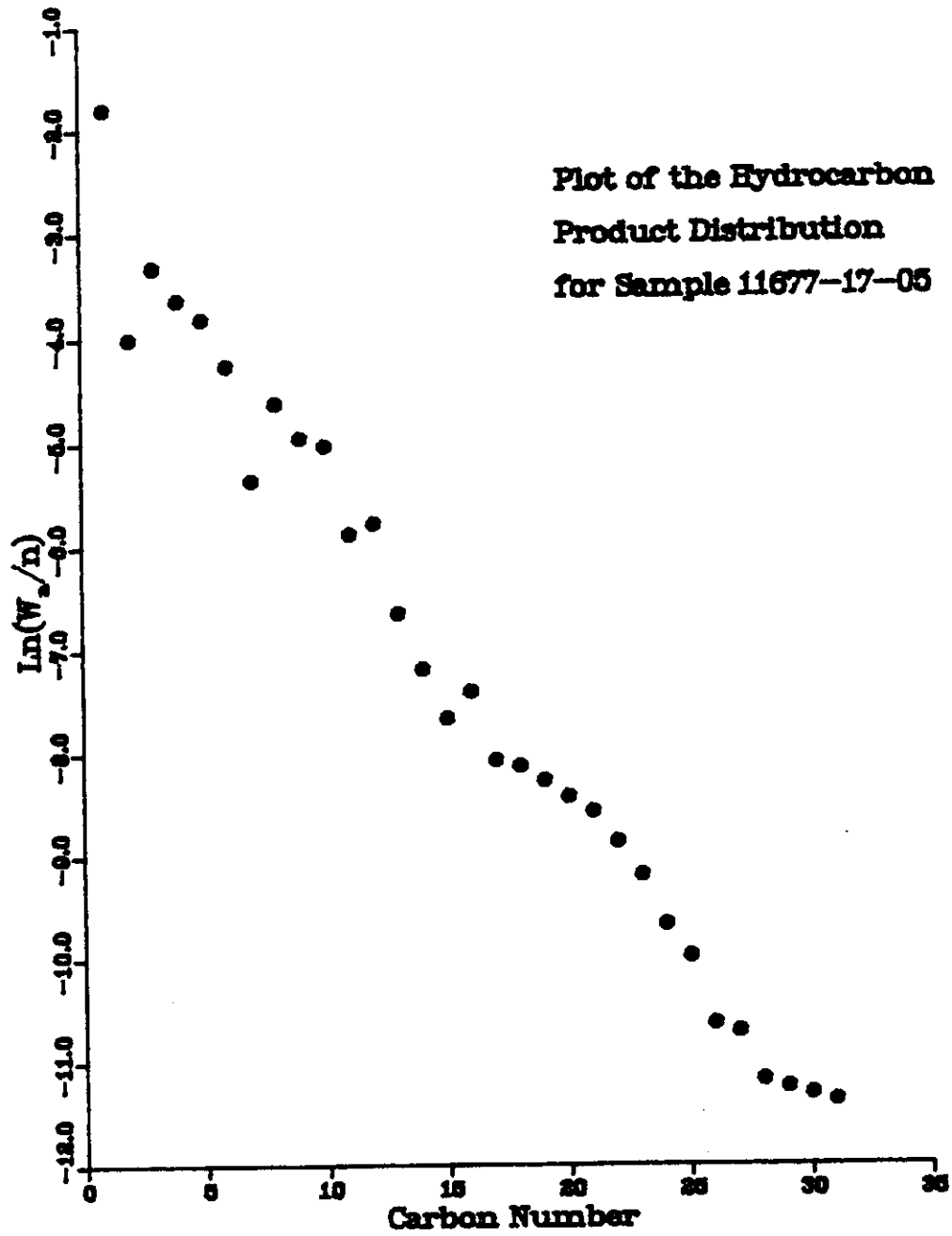


Fig. 76

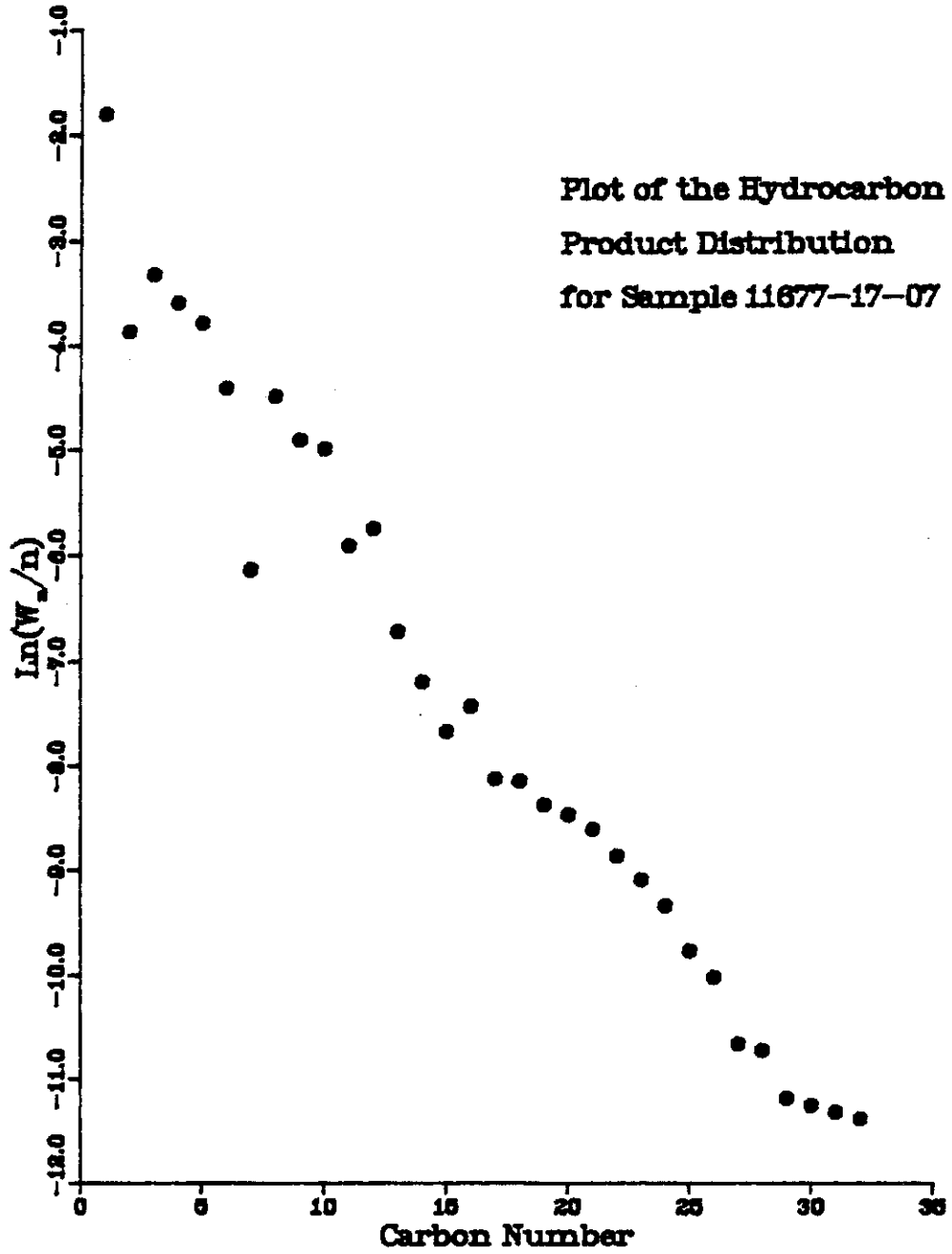


Table 11

RESULT OF SYNGAS OPERATION

RUN NO. 11677-17
 CATALYST CoThX4U103+U101 11684-92 250 CC 108.GM (111.7AFTER RUN +3.7G)
 FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11677-17-01	677-17-02	677-17-03	677-17-04	677-17-05
FEED H2:CO:AR	49:50:0	49:50:0	49:50:0	49:50:0	49:50:0
HRS ON STREAM	6.5	25.0	48.5	55.0	72.5
PRESSURE,PSIG	292	290	291	294	291
TEMP. C	258	263	258	261	260
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	6.50	25.00	23.50	6.50	24.00
EFFLNT GAS LITER	394.45	1445.45	1320.65	367.25	1366.00
GM AQUEOUS LAYER	21.66	83.32	96.44	25.47	94.03
GM OIL	1.18	4.53	11.26	2.86	10.56
MATERIAL BALANCE					
GM ATOM CARBON %	90.85	99.62	93.31	96.76	94.55
GM ATOM HYDROGEN %	102.17	96.23	97.48	98.12	97.83
GM ATOM OXYGEN %	95.22	98.91	96.87	97.84	97.44
RATIO CHX/(H2O+CO2)	0.7083	1.0455	0.8008	0.9385	0.8339
RATIO X IN CHX	2.6247	2.4956	2.4210	2.4281	2.4451
USAGE H2/CO PRODT	2.6396	2.0228	2.2979	2.1024	2.2359
FEED H2/CO FRM EFFLNT	1.0892	0.9355	1.0118	0.9821	1.0021
RESIDUAL H2/CO RATIO	0.8792	0.7082	0.7648	0.7372	0.7629
RATIO CO2/(H2O+CO2)	0.0165	0.0628	0.0392	0.0536	0.0479
K SHIFT IN EFFLNT	0.0147	0.0474	0.0312	0.0417	0.0384
SPECIFIC ACTIVITY SA	0.2287	0.3679	0.3908	0.3920	0.3557
CONVERSION					
ON CO %	11.93	17.29	16.11	17.94	16.24
ON H2 %	28.91	37.39	36.59	38.40	36.23
ON CO+H2 %	20.78	27.00	26.41	28.08	26.25
PRDT SELECTIVITY,WT %					
CH4	21.20	17.91	15.51	15.71	16.67
C2 HC'S	5.74	4.36	3.73	3.56	3.67
C3H8	12.22	7.66	5.46	5.90	5.57
C3H6=	5.44	5.11	5.08	5.02	5.15
C4H10	8.21	5.90	4.30	4.42	4.21
C4H8=	5.92	6.68	6.42	6.46	6.33
C5H12	7.03	6.09	4.47	4.90	4.96
C5H10=	4.27	6.41	5.95	5.12	6.08
C6H14	6.22	6.11	4.55	4.83	4.65
C6H12= & CYCLO'S	1.41	3.98	3.87	3.98	3.83
C7+ IN GAS	14.95	24.94	26.03	28.36	25.62
LIQ HC'S	7.39	4.86	14.64	11.73	13.25
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 11 (continued)

SUB-GROUPING					
C1 -C4	58.73	47.62	40.49	41.08	41.60
C5 -420 F	37.94	50.19	51.61	52.41	51.04
420-700 F	3.15	2.07	7.49	5.91	6.67
700-END PT	0.17	0.11	0.41	0.60	0.68
C5+-END PT	41.27	52.38	59.51	58.92	58.40
ISO/NORMAL MOLE RATIO					
C4	0.1774	0.1141	0.0859	0.0934	0.0801
C5	0.2726	0.1223	0.0987	0.0990	0.0919
C6	0.7043	0.2230	0.1617	0.1589	0.1576
C4=	0.0528	0.0799	0.0890	0.0898	0.0915
PARAFFIN/OLEFIN RATIO					
C3	2.1433	1.4316	1.0266	1.1213	1.0317
C4	1.3388	0.8520	0.6469	0.6602	0.6414
C5	1.6003	0.9237	0.7306	0.9299	0.7932
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.6038	0.6499	0.7268	0.7384	0.7423
RATIO CH4/(1-A)**2	1.3502	1.4610	2.0772	2.2962	2.5093
LIQ HC COLLECTION					
PHYS. APPEARANCE		CLDY	CLDY		CLDY BL
DENSITY		0.7524	0.7545		0.7586
N, REFRACTIVE INDEX		1.4264	1.4270		1.4272
SIMULT'D DISTILATN					
10 WT % @ DEG F		303	305		305
16		332	342		342
50		415	436		447
84		517	585		614
90		546	626		656
RANGE(16-84 %)		185	243		272
WT % @ 420 F	55.00	55.00	46.00	44.50	44.50
WT % @ 700 F	97.66	97.66	97.17	94.88	94.88

NEW FORMAT AUG 29,84

Table 12

RESULT OF SYNGAS OPERATION

RUN NO. 11677-17
 CATALYST CoThX4U103+U101 11684-92 250 CC 108.GM (111.7AFTER RUN +3.7G)
 FEED H₂:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 108.GHSV

RUN & SAMPLE NO.	11677-17-06	677-17-07
	=====	=====
FEED H ₂ :CO:AR	49:50: 0	49:50: 0
HRS ON STREAM	79.0	96.5
PRESSURE,PSIG	296	293
TEMP. C	258	258
FEED CC/MIN	1260	1260
HOURS FEEDING	6.50	24.00
EFFLNT GAS LITER	383.85	1398.15
GM AQUEOUS LAYER	23.98	88.53
GM OIL	2.64	9.76
MATERIAL BALANCE		
GM ATOM CARBON %	95.99	94.82
GM ATOM HYDROGEN %	99.82	98.50
GM ATOM OXYGEN %	98.76	97.85
RATIO CHX/(H ₂ O+CO ₂)	0.8332	0.8179
RATIO X IN CHX	2.4264	2.4463
USAGE H ₂ /CO PRODT	2.2442	2.2601
FEED H ₂ /CO FRM EFFLNT	1.0071	1.0060
RESIDUAL H ₂ /CO RATIO	0.7860	0.7822
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0434	0.0466
K SHIFT IN EFFLNT	0.0357	0.0382
SPECIFIC ACTIVITY SA	0.3462	0.3516
CONVERSION		
ON CO %	15.16	15.15
ON H ₂ %	33.79	34.03
ON CO+H ₂ %	24.51	24.61
PRDT SELECTIVITY,WT %		
CH ₄	16.00	16.51
C ₂ HC'S	3.59	4.20
C ₃ H ₈	5.38	5.55
C ₃ H ₆ =	5.45	5.25
C ₄ H ₁₀	4.29	4.42
C ₄ H ₈ =	6.52	6.60
C ₅ H ₁₂	4.62	4.86
C ₅ H ₁₀ =	6.10	6.52
C ₆ H ₁₄	4.52	4.91
C ₆ H ₁₂ = & CYCLO'S	3.52	2.42
C ₇ + IN GAS	27.16	25.67
LIQ HC'S	12.85	13.08
TOTAL	100.00	100.00

Table 12 (continued)

SUB-GROUPING		
C1 -C4	41.23	42.52
C5 -420 F	51.57	50.15
420-700 F	6.31	6.42
700-END PT	0.89	0.91
C5+-END PT	58.77	57.48
ISO/NORMAL MOLE RATIO		
C4	0.0847	0.0854
C5	0.0890	0.0850
C6	0.1599	0.1632
C4=	0.0894	0.0915
PARAFFIN/OLEFIN RATIO		
C3	0.9429	1.0093
C4	0.6353	0.6462
C5	0.7363	0.7245
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))		0.7522
RATIO CH4/(1-A)**2		2.6885
LIQ HC COLLECTION		
PHYS. APPEARANCE		CLDY BL
DENSITY		0.7587
N, REFRACTIVE INDEX		1.4272
SIMULT'D DISTILATN		
10 WT % @ DEG F		305
16		342
50		450
84		627
90		673
RANGE(16-84 %)		285
WT % @ 420 F	44.00	44.00
WT % @ 700 F	93.08	93.08

NEW FORMAT AUG 29,84

VI. Run 5 (11677-13) with Catalyst 7 (Cu/Zn/Al+UCC-101

This is strictly a water gas shift catalyst with no Fischer-Tropsch-active metal component. The UCC-101 component is intended as a diluent.

The water gas shift component, consisting of Zn:Cu:Al in a weight ratio of 2:1:0.1, was prepared by adding base to a stirred, room-temperature solution of the cations. The dried precipitate was calcined in air at 400C, and formed into a 1/8-inch extrudate containing 10 percent of the water gas shift component and 15 percent SiO₂ binder, with UCC-101 making up the balance. Then, even though it contained no Fischer-Tropsch component, the catalyst was activated in hydrogen at 350C to simulate what would happen if it were part of a Fischer-Tropsch catalyst.

Detailed material balances appear in Table 13.

The catalyst was fed a mixture of water, carbon monoxide and hydrogen in a volume ratio of 3:3:1 at 525 GHSV. It was rather active initially, shifting more than 50 percent of the CO+H₂O to CO₂+H₂, but then deactivated rapidly at a rate of almost 0.6 percent per hour.

Although it contained only 10 percent water gas shift component, this catalyst was sufficiently active that, in combination with a Fischer-Tropsch catalyst, it should produce some significant water gas shift activity at least in the first few samples.

Table 13

RESULT OF WATER GAS SHIFT REACTION

RUN NO. 11677-13
 CATALYST Cu/Zn/Al & UCC-101 #11684-67C 80 CC 31.4 GM
 FEED H₂O:CO:H₂ OF 3:3:1 @ 14CC/HR & 400 CC(CO+H₂)/MN, TOTAL 525 GHSV

	11677-13-01	677-13-02	677-13-04	677-13-06	677-13-08
	=====	=====	=====	=====	=====
FEED H ₂ O:CO:H ₂	31:30:10	31:30:10	31:30:10	31:30:10	31:30:10
HRS ON STREAM	3.0	22.0	46.17	72.0	94.26
PRESSURE, PSIG	303	303	301	298	299
TEMP. C	259	260	260	260	260
FEED (CO+H ₂)CC/MN	400	400	400	400	400
FEED WATER CC/HR	14	14	14	14	14
HOURS FEEDING	3.0	22.0	24.17	25.83	22.25
EFFLNT GAS LITER	112.50	761.75	765.56	727.88	532.31
GM AQUEOUS LAYER	17.20	126.13	200.02	277.94	281.04
MATERIAL BALANCE					
GM MOLE H ₂ O %	97.64	90.44	89.48	90.20	98.34
GM MOLE CO %	98.03	105.28	108.55	107.90	94.17
GM MOLE H ₂ %	151.92	104.77	105.92	103.25	90.18
K SHIFT IN EFFLNT	2.9174	1.4936	0.343	0.0601	0.0240
CONVERSION					
ON H ₂ O %	54.08	50.75	30.21	11.43	5.58
ON CO %	56.38	45.63	26.06	10.00	6.10
ON H ₂ O+CO %	55.21	48.05	27.98	10.67	5.83

VII. Run 6 (11723-11) with Catalyst 6 (Co/Th/Cu+UCC-101+Cu/Zn/Al)

The water gas shift component Cu/Zn/Al was found to be active when tested separately in the previous run. However, Catalyst 10 of the Third Annual Report, which contained the same component, was found to have no water gas shift activity when tested with a syngas feed. One possible explanation is that the water gas shift catalyst was deactivated by the high reduction temperature required to activate the Fischer-Tropsch component.

The effect of adding copper to iron, to lower the temperature at which iron can be reduced, is well recognized and represents the state of the art in iron Fischer-Tropsch catalysts. Copper is known to do the same for cobalt catalysts as well, but is not ordinarily used since it also usually impairs the catalyst's stability. The prime objective of this test, however, was high initial Fischer-Tropsch and water gas shift activity; stability was not a major concern.

The metal component was formed by precipitating cobalt and copper with a base from a solution of their nitrate salts. The precipitated metal oxides were then treated with thorium and subsequently mixed with UCC-101 and with the same Cu/Zn/Al water gas shift component used in Catalyst 5. After being formed as a 1/8-inch, SiO₂-bonded extrudate, the final catalyst contained 10 percent cobalt and about 7 percent of the water gas shift component.

Since a temperature-programed reduction showed that the catalyst could be reduced at 260C, it was reduced in hydrogen at 260C prior to being contacted with the CO+H₂ feed at that same temperature.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 77-80. Simulated distillations of the C₅⁺ product are plotted in Figs. 81-82. Carbon number product distributions are plotted in Figs. 83-84. Chromatograms from simulated distillations are reproduced in Figs. 85-86. Detailed material balances appear in Table 14.

The initial conversion was fairly high, with about 63 percent of CO+H₂ converted, but as expected it declined rapidly. The water gas shift activity, although higher than that of the first four catalysts in this Report, was nonetheless inferior to that of other catalysts prepared in the same way as this one but with neither the copper nor the water gas shift component. The initial usage ratio was 1.58:1, and only 28 percent of the oxygen was rejected as CO₂, whereas with the catalyst in Run 10112-15 (Co/Th+UCC-101) the corresponding values were 1.23:1 and 37 percent respectively. If the water gas shift component in this catalyst was fully active, its activity should have been much higher, with at least half the oxygen rejected as CO₂.

Both the product selectivity and product quality were poor, as the figures and table demonstrate. The water gas shift component was inactive even though it had been spared the high re-

duction temperature used in earlier tests.

As to why these Fischer-Tropsch water gas shift catalysts are so inactive, two possible explanations suggest themselves. First, that one or more components may be migrating from the Fischer-Tropsch constituent, even at reaction temperatures, to deactivate the water gas shift constituent. Second, that intermediate products from the Fischer-Tropsch syntheses, such as small olefins, may be adsorbing onto the water gas shift component and deactivating it.

RUN 11723-11

1:1 H₂:CO
300 PSIG
260°C

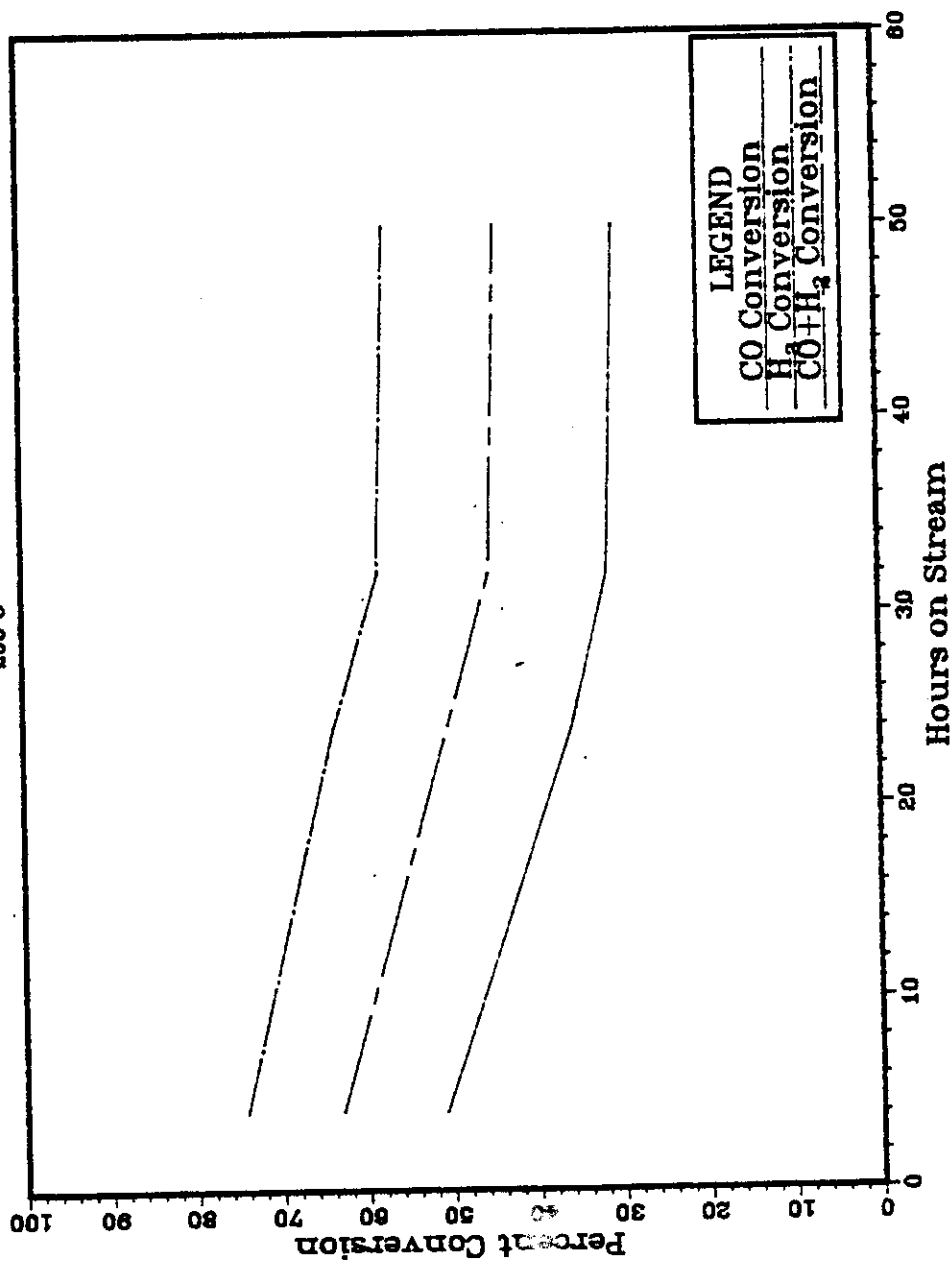


Fig. 77

Fig. 78

RUN 11723-11

1:1 H₂:CO
300 PSIG
280°C

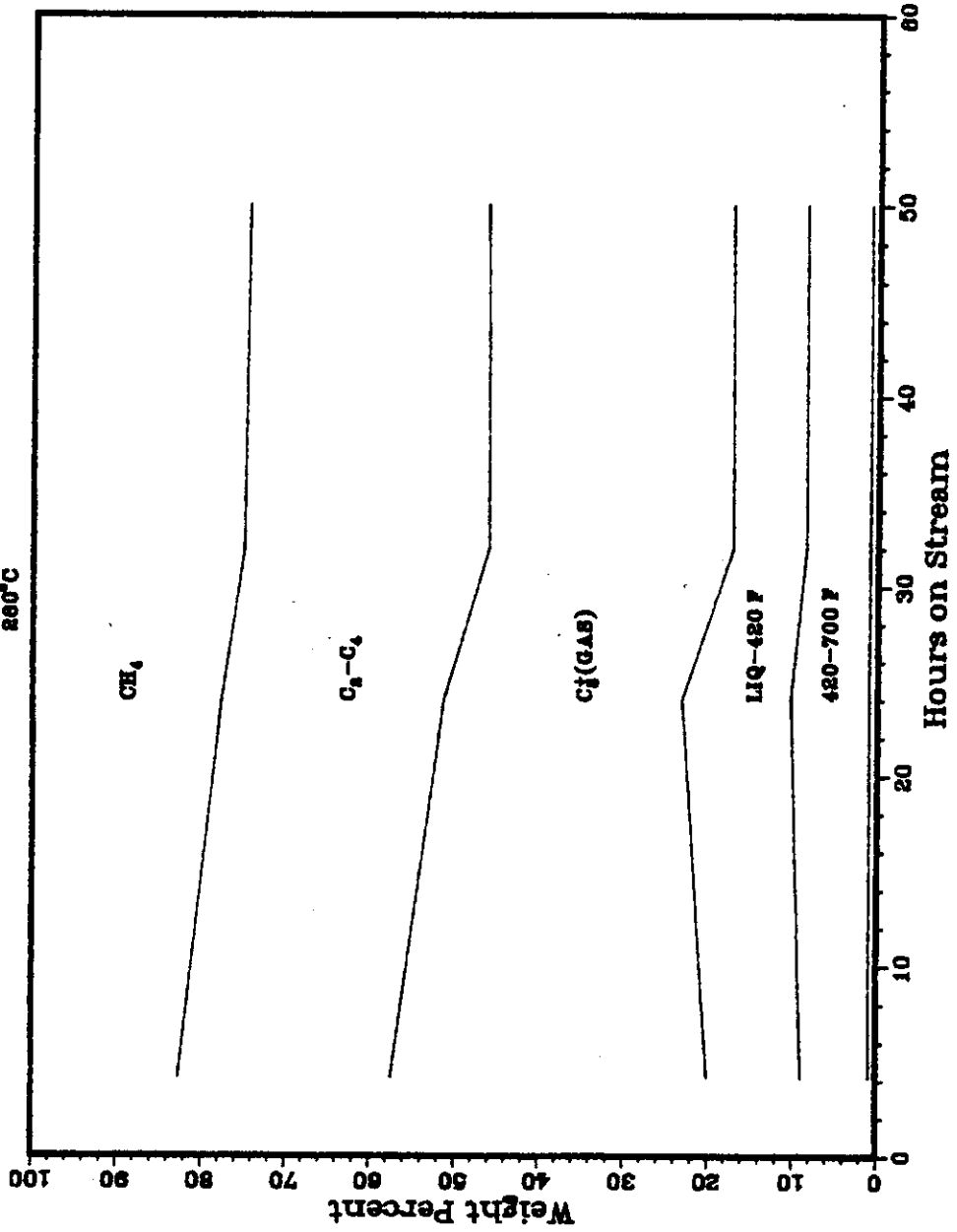


Fig. 79

RUN 11723--11

1:1 H₂:CO
300 PSIG
880°C

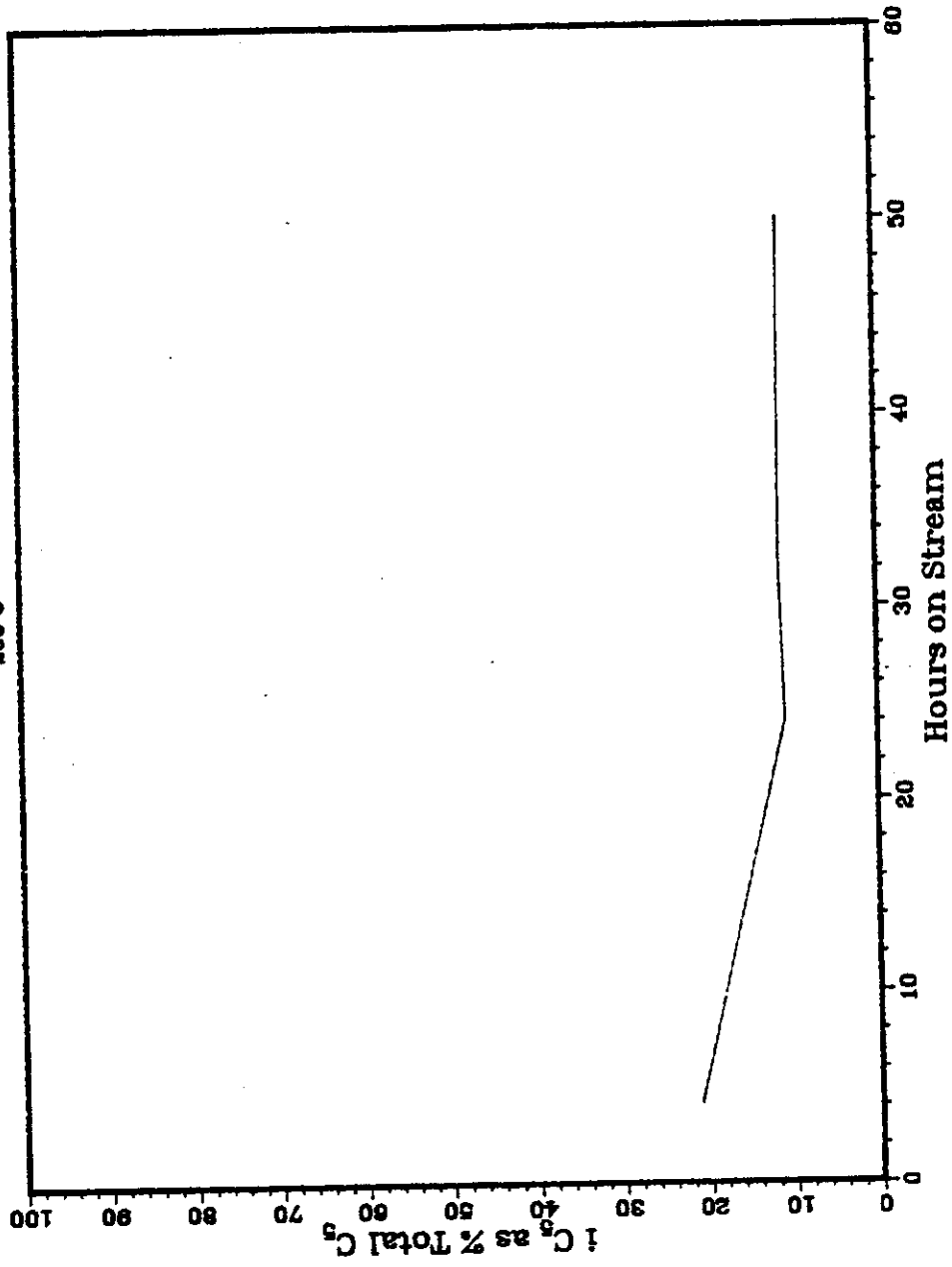


Fig. 80

RUN 11723-11

1:1 H₂:CO
300 PSIG
260°C

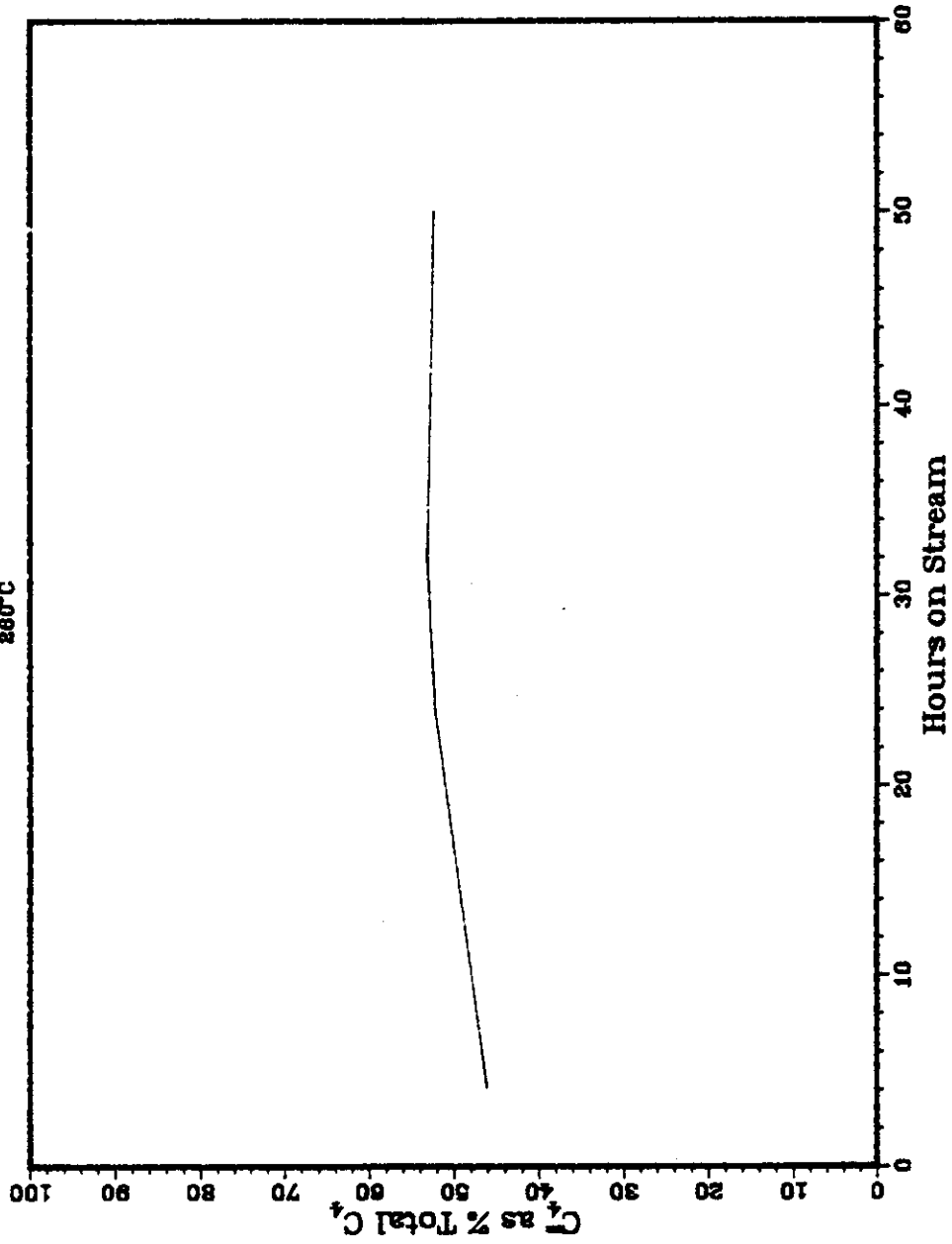


Fig. 81

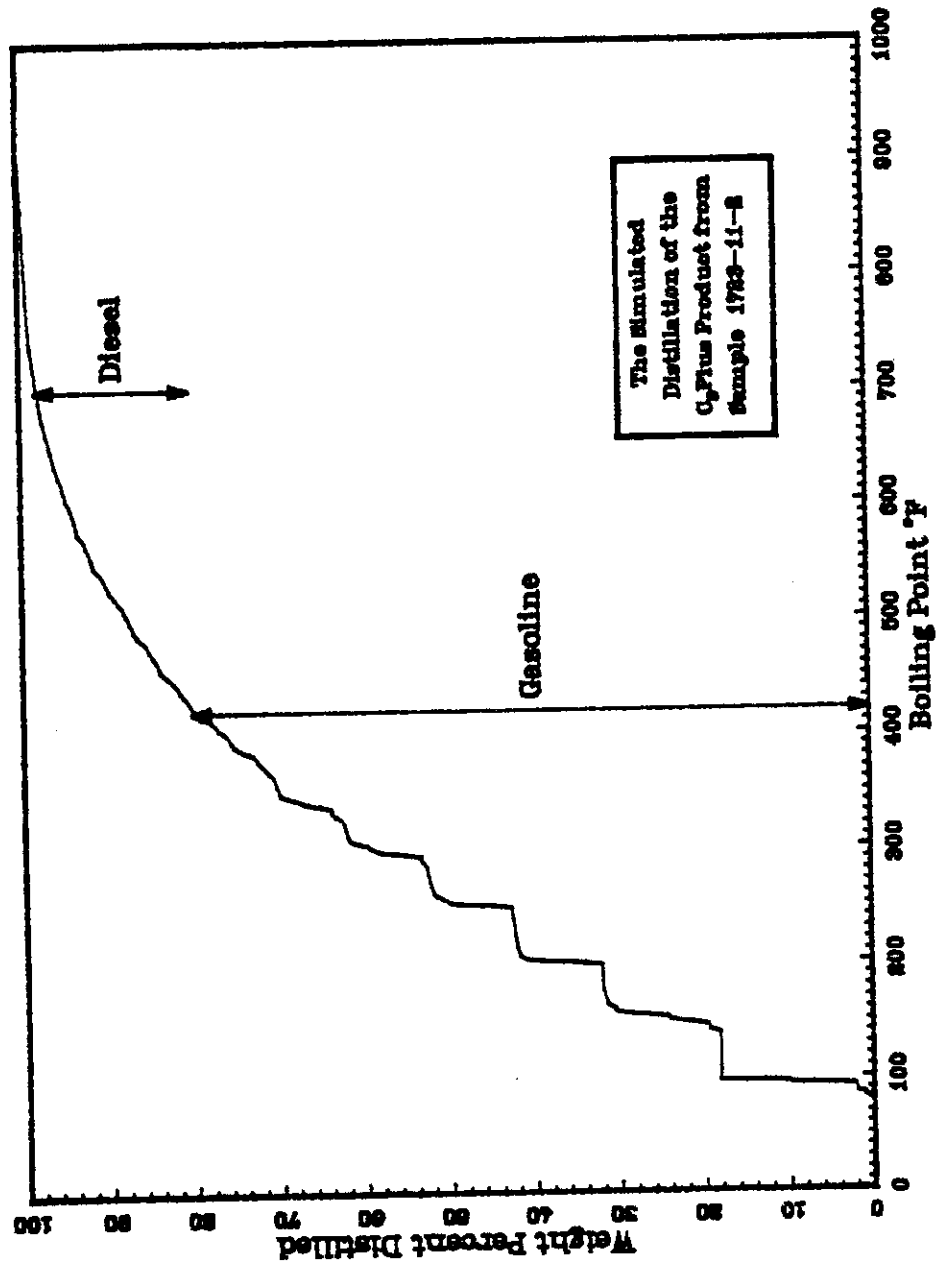


Fig. 82

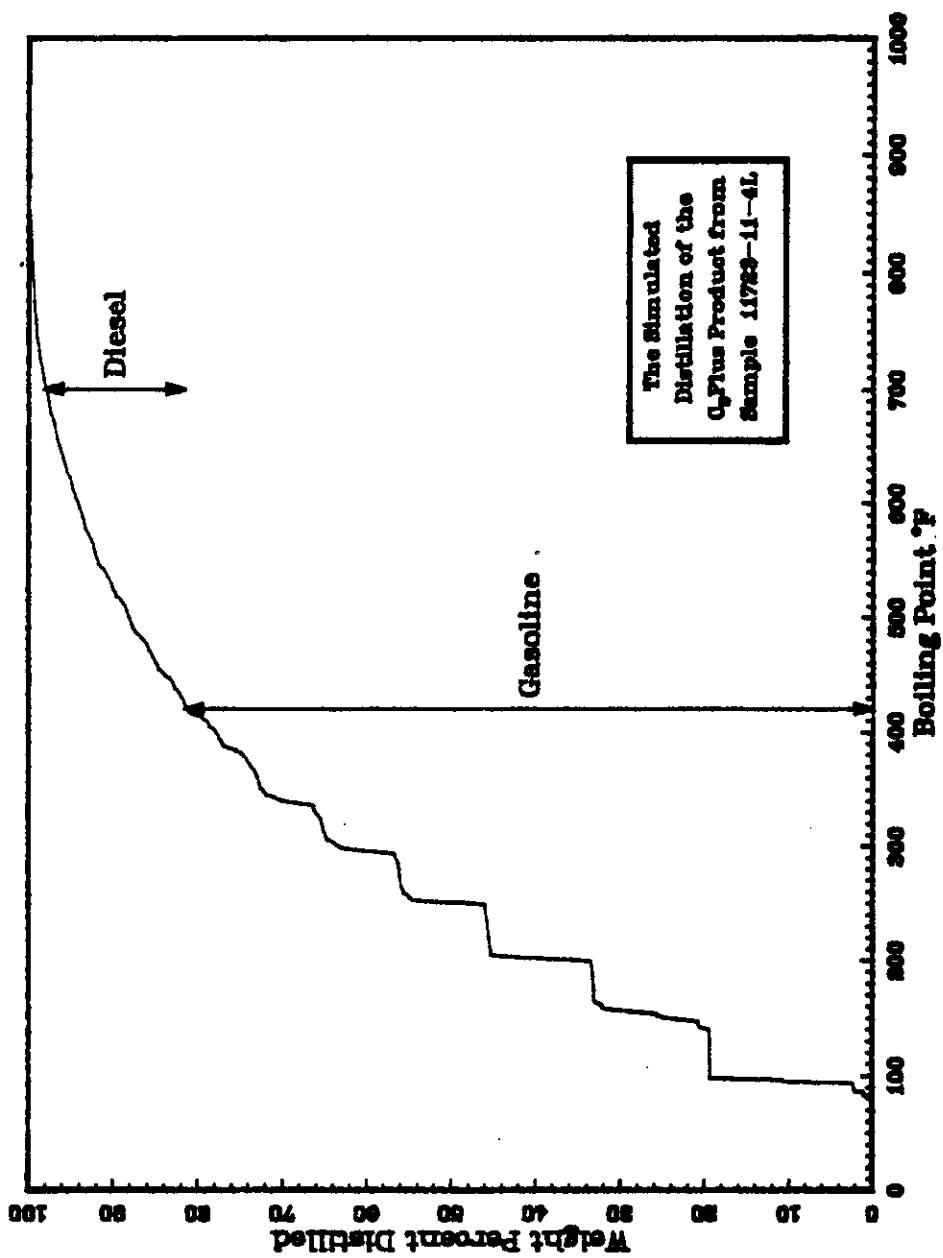


Fig. 83

