

TABLE 42

RESULT OF SYNGAS OPERATION

RUN NO. 10112-22

CATALYST CO/TH/X4+UCC-108 10252-90C 80CC 39.9GM (42.6 AFTER RUN +2.7G)

FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10112-22-07 112-22-09 112-22-10 112-22-11 112-22-12

	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	90.5	115.5	122.5	139.0	145.8
PRESSURE, PSIG	302	298	305	306	306
TEMP. C	271	271	272	271	272
FEED CC/MIN	400	400	543	600	651
HOURS FEEDING	24.50	25.00	7.00	23.50	6.75
EFFLNT GAS LITER	286.05	298.95	128.00	470.95	180.50
GM AQUEOUS LAYER	53.98	53.30	17.85	64.33	18.85
GM OIL	22.36	20.73	5.65	20.37	4.89
MATERIAL BALANCE					
GM ATOM CARBON %	99.33	99.22	98.38	96.43	107.53
GM ATOM HYDROGEN %	97.99	97.01	94.19	93.03	102.16
GM ATOM OXYGEN %	101.05	100.90	99.37	97.51	107.97
RATIO CHX/(H ₂ O+CO ₂)	0.9580	0.9574	0.9691	0.9653	0.9846
RATIO X IN CHX	2.4463	2.4660	2.4677	2.4788	2.4857
USAGE H ₂ /CO PRODT	1.3748	1.3879	1.5298	1.5285	1.6130
RATIO CO ₂ /(H ₂ O+CO ₂)	0.3478	0.3443	0.2726	0.2746	0.2384
K SHIFT IN EFFLNT	0.27	0.27	0.21	0.22	0.20
CONVERSION					
ON CO %	53.64	51.74	40.33	40.12	32.65
ON H ₂ %	75.96	74.64	65.25	64.45	55.78
ON CO+H ₂ %	64.72	63.06	52.52	52.07	43.92
PROT SELECTIVITY, WT %					
CH ₄	19.34	20.21	20.58	21.05	21.49
C ₂ HC'S	4.01	4.27	4.23	4.62	4.51
C ₃ H ₈	4.27	4.35	4.00	3.88	3.96
C ₃ H ₆ =	3.57	3.68	4.33	4.23	5.11
C ₄ H ₁₀	2.62	2.65	2.55	2.45	2.52
C ₄ H ₈ =	5.65	5.72	6.19	6.09	6.58
C ₅ H ₁₂	2.53	2.53	2.39	2.38	2.46
C ₅ H ₁₀ =	5.56	5.49	5.79	5.84	6.21
C ₆ H ₁₄	2.55	2.59	2.45	2.50	2.46
C ₆ H ₁₂ = & CYCLO'S	4.57	4.57	4.81	4.85	4.79
C ₇ + IN GAS	12.69	13.26	15.85	15.33	17.95
LIQ HC'S	32.66	30.68	26.82	26.78	21.93
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	39.45	40.88	41.89	42.32	44.18
C5 -420 F	45.53	44.64	44.38	43.97	44.01
420-700 F	13.12	12.54	11.64	11.62	9.86
700-END PT	1.91	1.94	2.09	2.09	1.94
C5+END PT	60.55	59.12	58.11	57.68	55.82
ISO/NORMAL MOLE RATIO					
C4	0.0347	0.0322	0.0402	0.0327	0.0400
C5	0.0950	0.0919	0.0876	0.0879	0.0870
C6	0.1305	0.1329	0.1099	0.1235	0.1130
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1407	1.1274	0.8818	0.8767	0.7393
C4	0.4483	0.4462	0.3980	0.3875	0.3701
C5	0.4422	0.4473	0.4013	0.3954	0.3858
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7931	0.7931		0.7946	
RATIO CH4/(1-A)**2	4.5178	4.7214		4.9892	
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL	CLR OIL		CLR OIL	
DENSITY	0.753	0.753		0.758	
N, REFRACTIVE INDEX	1.4256	1.4259		1.4280	
SIMULT'D DISTILATN					
10 WT % @ DEG F	259	260		287	
16	296	300		304	
50	410	413		428	
84	583	591		619	
90	642	650		674	
RANGE(16-84 %)	287	291		315	
WT % @ 420 F	54.00	52.80	48.80	48.80	46.17
WT % @ 700 F	94.16	93.69	92.20	92.20	91.14

TABLE 43

RESULT OF SYNGAS OPERATION

RUN NO. 10112-22
 CATALYST CO/TH/X4+UCC-108 10252-90C 80CC 39.9GM (42.6 AFTER RUN +2.7G)
 FEED H₂:CO:ARGON OF 50:50: 0 @ 800 CC/MN OR 600 GHSV

RUN & SAMPLE NO.	10112-22-13	112-22-14	112-22-15	112-22-16	112-22-17
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	163.0	170.0	187.0	194.5	211.0
PRESSURE, PSIG	304	304	305	297	302
TEMP. C	272	272	281	281	281
FEED CC/MIN	800	800	800	800	800
HOURS FEEDING	24.00	7.00	24.00	7.50	24.00
EFFLNT GAS LITER	707.05	213.00	678.25	210.75	673.70
GM AQUEOUS LAYER	77.96	25.29	86.72	27.26	87.22
GM OIL	20.22	6.09	20.89	6.46	20.67
MATERIAL BALANCE					
GM ATOM CARBON %	96.53	99.70	102.92	102.66	100.76
GM ATOM HYDROGEN %	93.32	98.14	97.70	98.32	97.28
GM ATOM OXYGEN %	97.73	102.08	102.87	101.80	100.90
RATIO CHX/(H ₂ O+CO ₂)	0.9553	0.9183	1.0014	1.0265	0.9955
RATIO X IN CHX	2.4931	2.4840	2.5606	2.5526	2.5580
USAGE H ₂ /CO PRODT	1.6155	1.6323	1.5010	1.5263	1.5371
RATIO CO ₂ /(H ₂ O+CO ₂)	0.2338	0.2184	0.3119	0.3023	0.2915
K SHIFT IN EFFLNT	0.19	0.18	0.25	0.24	0.23
CONVERSION					
ON CO %	33.10	33.13	41.81	42.02	40.83
ON H ₂ %	56.35	56.92	66.08	66.29	65.12
ON CO+H ₂ %	44.53	44.93	53.63	53.89	52.76
PRODT SELECTIVITY, WT %					
CH ₄	21.76	21.43	24.75	24.37	24.77
C ₂ HC'S	4.90	4.56	5.02	4.90	4.93
C ₃ H ₈	3.84	3.83	4.62	4.67	4.54
C ₃ H ₆ =	4.82	4.88	4.58	4.66	4.83
C ₄ H ₁₀	2.45	2.46	2.76	2.75	2.64
C ₄ H ₈ =	6.34	6.39	6.47	6.50	6.23
C ₅ H ₁₂	2.43	2.38	2.62	2.57	2.49
C ₅ H ₁₀ =	6.07	6.20	6.30	6.24	6.28
C ₆ H ₁₄	2.57	2.54	2.68	2.63	2.60
C ₆ H ₁₂ = & CYCLO'S	4.88	4.81	4.80	5.03	4.54
C ₇ + IN GAS	17.07	17.77	17.00	17.73	17.37
LIQ HC'S	22.88	22.75	18.41	17.94	18.78
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	44.11	43.56	48.20	47.85	47.94
C5 -420 F	43.57	44.95	42.51	43.14	42.63
420-700 F	10.29	9.52	7.71	7.52	7.87
700-END PT	2.03	1.97	1.59	1.49	1.56
C5-END PT	55.89	56.44	51.80	52.15	52.06
ISO/NORMAL MOLE RATIO					
C4	0.0355	0.0377	0.0417	0.0407	0.0416
C5	0.0915	0.0853	0.1047	0.1090	0.1092
C6	0.1058	0.1154	0.1563	0.1729	0.1749
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.7619	0.7492	0.9621	0.9560	0.8987
C4	0.3725	0.3724	0.4119	0.4088	0.4090
C5	0.3889	0.3731	0.4038	0.4013	0.3861
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7948		0.7894		0.7919
RATIO CH4/(1-A)**2	5.1693		5.5804		5.7171
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		CLR OIL
DENSITY	0.761		0.758		0.758
N _D REFRACTIVE INDEX	1.4289		1.4281		1.4282
SIMULT'D DISTILATN					
10 WT % @ DEG F	299		285		290
16	324		303		306
50	437		423		421
84	630		625		616
90	687		683		677
RANGE(16-84 %)	306		322		310
WT % @ 420 F	46.17	49.50	49.50	49.80	49.80
WT % @ 700 F	91.14	91.36	91.36	91.69	91.69

VIII. Run 7 (11677-12) with Catalyst 7 (Cu/Zn/Al₂O₃)

This is strictly a water gas shift catalyst, not a Fischer-Tropsch catalyst. The purpose is to isolate the activity of the water gas shift component to obtain a benchmark for comparison with its activity when incorporated into a Fischer-Tropsch catalyst.

The copper, zinc and alumina were precipitated from aqueous solutions of their nitrate salts by addition of ammonium bicarbonate. The final catalyst contained 10 weight percent Al₂O₃ and a 2:1 mole ratio of zinc to copper.

Detailed material balances appear in Table 44.

The catalyst was fed a 3:3:1 volume mixture of H₂O:CO:H₂. There was observable activity initially, followed by rapid deactivation with a loss of 1 percentage point of activity every 2.4 hours on stream.

TABLE 44

RESULTS OF WATER GAS SHIFT REACTION

RUN NO. 11677-12
 CATALYST CU/ZN/AL & USS-101 #11684-670 80.00 31.1 GM
 FEED H₂O:CO:H₂ OF 31:30:10 1400/MM (100(CO+H₂)/MM, TOTAL 525 GHSV

	11677-12-01	677-12-03	677-12-05	677-12-06	677-12-07
	=====				
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	4.5	31.5	72.1	77.9	95.5
PRESSURE, PSIG	302	304	304	303	303
TEMP. °C	262	259	259	259	259
FEED (CO+H ₂) CC/MM	400	400	400	400	400
FEED WATER CC/HF	14	14	14	14	14
HOURS FEEDING	4.5	7.0	23.25	5.78	24.42
EFFLNT GAS LITER	149.95	227.10	715.90	169.89	700.05
GM AQUEOUS LAYER	26.16	55.48	214.94	66.01	278.67
MATERIAL BALANCE					
GM MOLE H ₂ O %	95.05	101.97	92.48	105.67	98.88
GM MOLE CO %	97.17	100.16	109.15	104.43	107.25
GM MOLE H ₂ %	94.04	97.10	101.73	99.86	100.88
K SHIFT IN EFFLNT	2.08	0.944	0.229	0.166	0.0887
CONVERSION					
ON H ₂ O %	52.67	41.10	25.07	19.85	14.43
ON CO %	53.93	43.77	22.23	21.03	13.92
ON H ₂ O+CO %	53.30	42.44	23.65	20.44	14.18

IX. Run 8 (11723-05) with Catalyst 8
(Co/Th+UCC-103+UCC-101+Cu/Zn)

This catalyst is the same as Catalyst 2, with the addition of a Cu/Zn water gas shift component. The latter was precipitated from an equimolar solution of copper and zinc chlorides by addition of sodium carbonate, and after calcining in air at 400C was physically mixed with the Co/Th+UCC-103+UCC-101. The mixture was then bonded with silica and formed as a 1/8-inch extrudate.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 165-168. Simulated distillations of the C₅⁺ product are plotted in Figs. 169-170. Carbon number product distributions are plotted in Figs. 171-174. Detailed material balances appear in Tables 45-46.

Conversion of the syngas was low initially at 39 percent, and dropped by one percentage point every 7 hours on stream. This is only about half the activity of Catalyst 6, which contained the same proportion of cobalt. The water gas shift activity was also much lower than usual, with only 3 percent of the oxygen rejected as CO₂ and a H₂:CO usage ratio of 2.2:1. With Catalyst 6, which also had low water gas shift activity, 6-9 percent of the oxygen was rejected as CO₂ and the H₂:CO usage ratio was 2:1.

The selectivity was also much lower than usual. Methane pro-

duction, initially 26 percent, was up to 32 percent at 90 hours on stream. Less than half the total product was C_5^+ hydrocarbons, nearly all of which was gasoline. The pentane was poorly isomerized and the C_4 hydrocarbons mostly paraffins. The Schulz-Flory plots are linear, but with the poor selectivity the methane was not in great excess.

The intended "water gas shift component" used in this catalyst had quite the opposite effect, almost eliminating the catalyst's water gas shift activity. Still further, it substantially impaired the F-T component's conversion, selectivity and stability.

RUN 11723-05

1:1 H₂:CO
300 PSIG
270°C

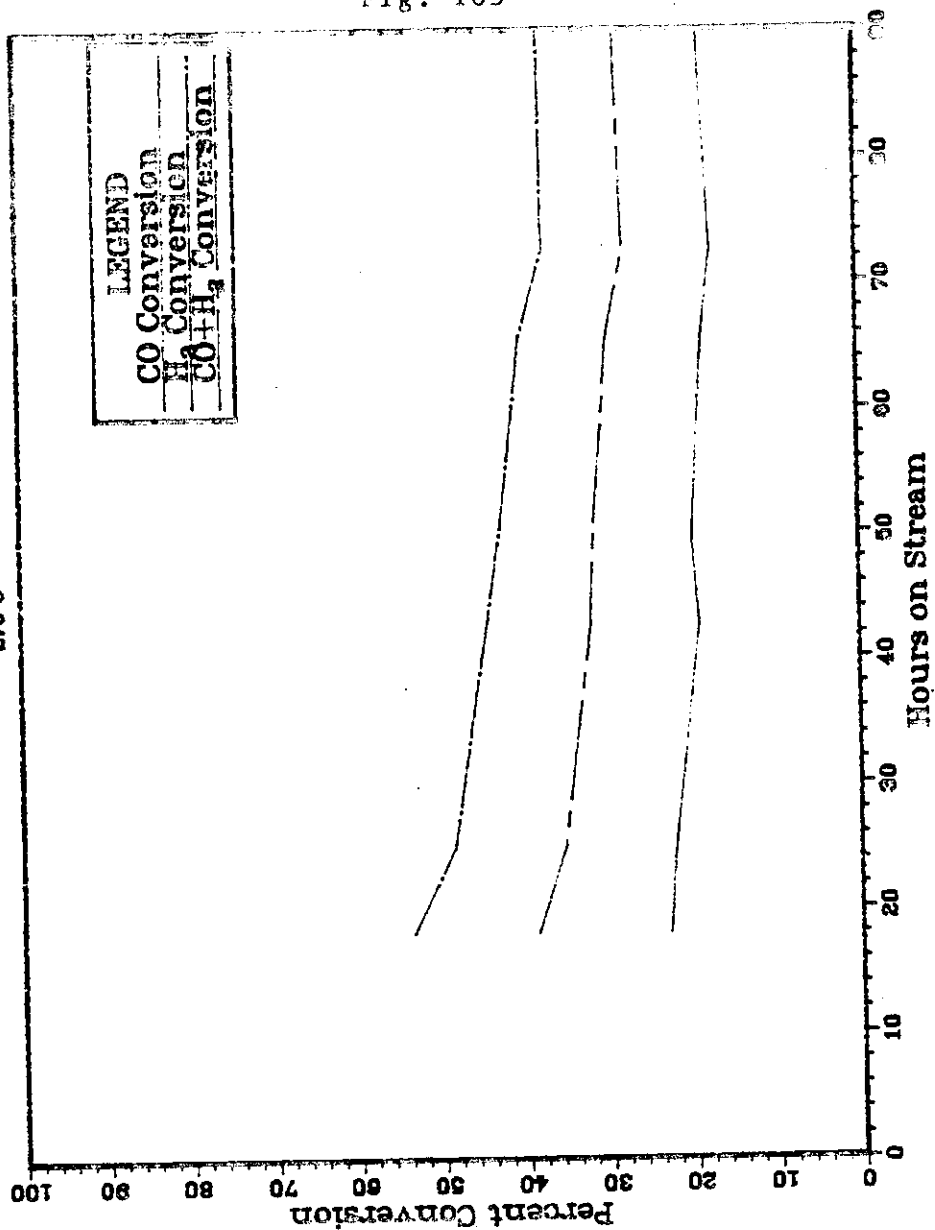
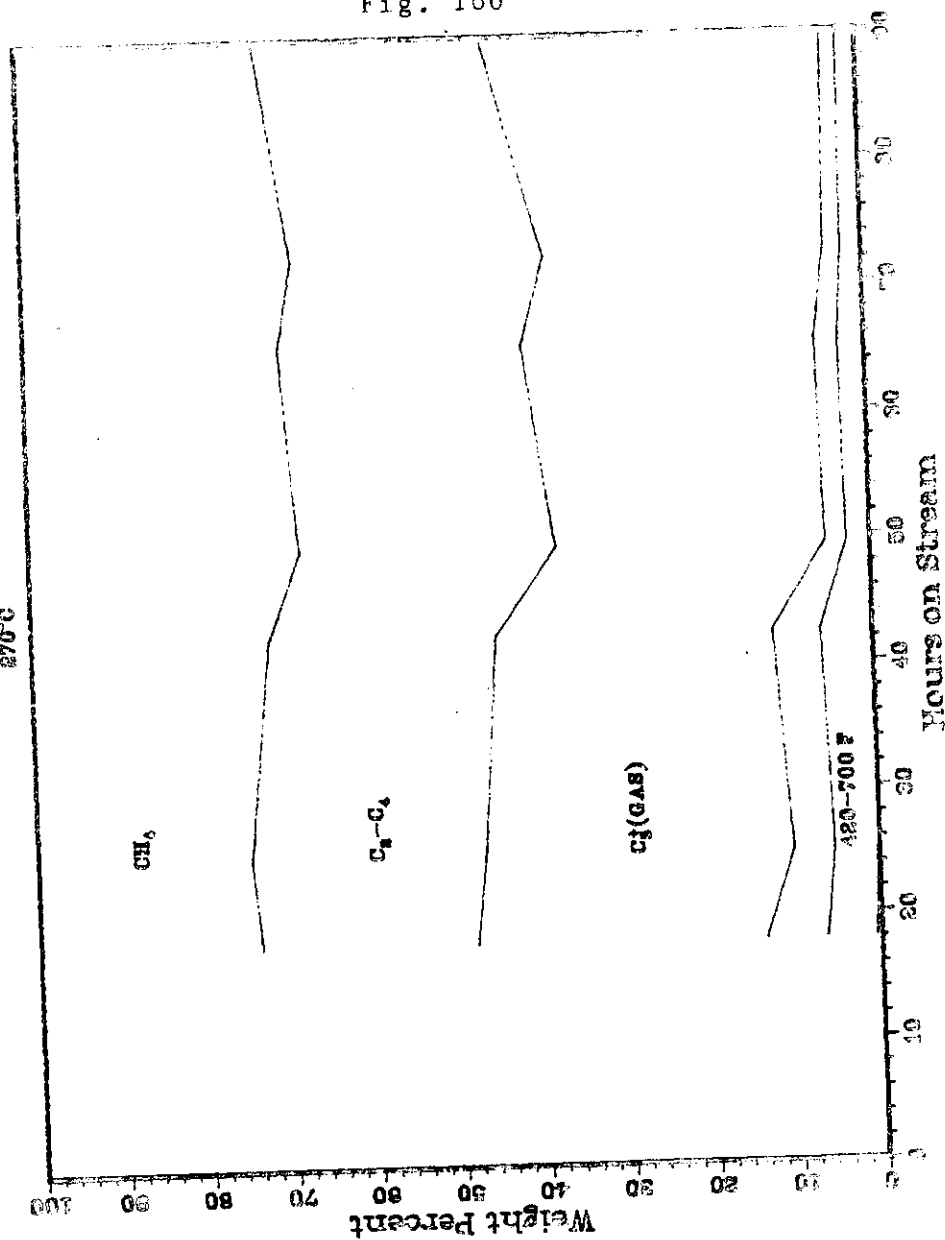


Fig. 165

RUN 11723-05

1:1 H₂:CO
300 PSIG
270°C

Fig. 166



RUN 11723--05

1:1 H₂:CO
300 PSIG
270°C

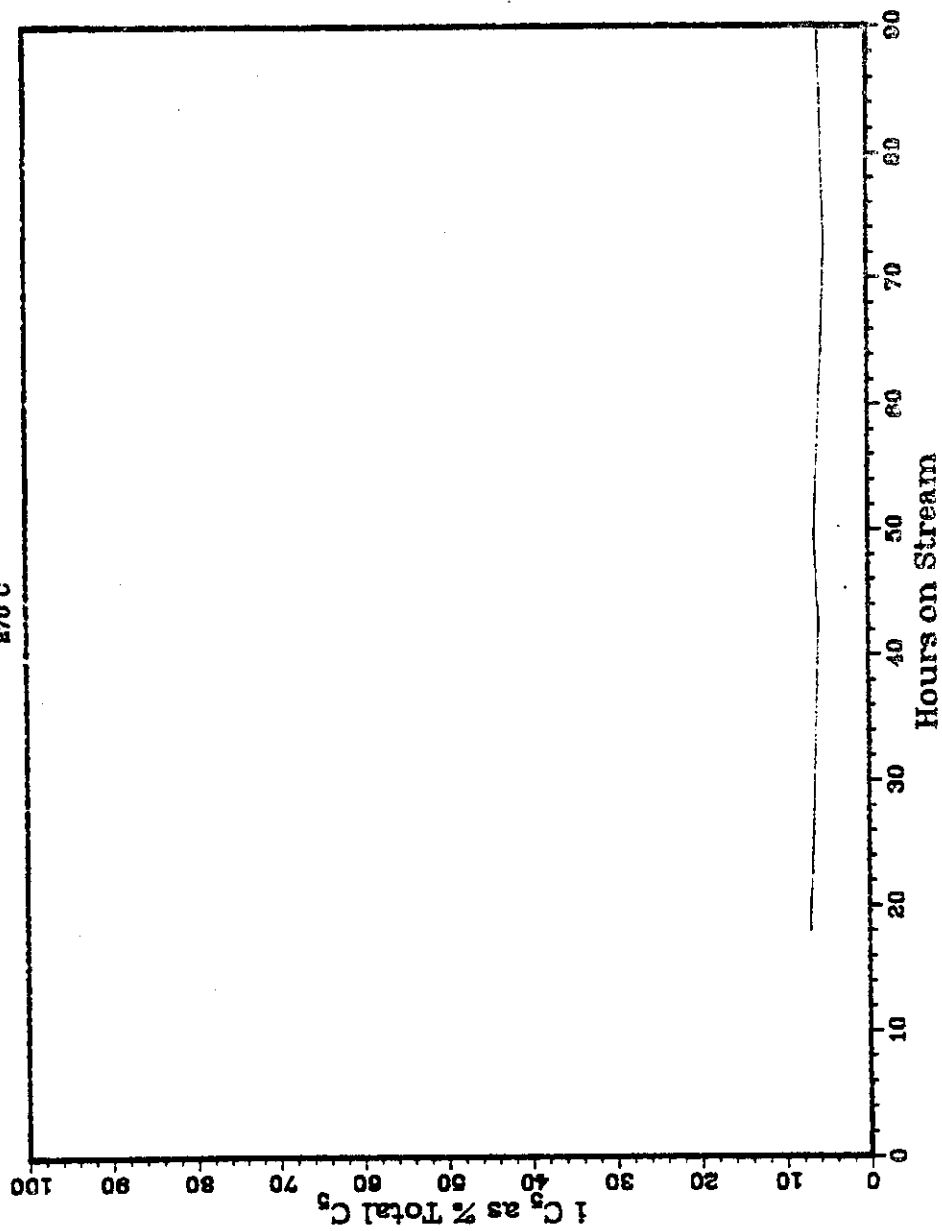


Fig. 167

RUN 11723-05

111 H₂CO
300 PSIG
270°C

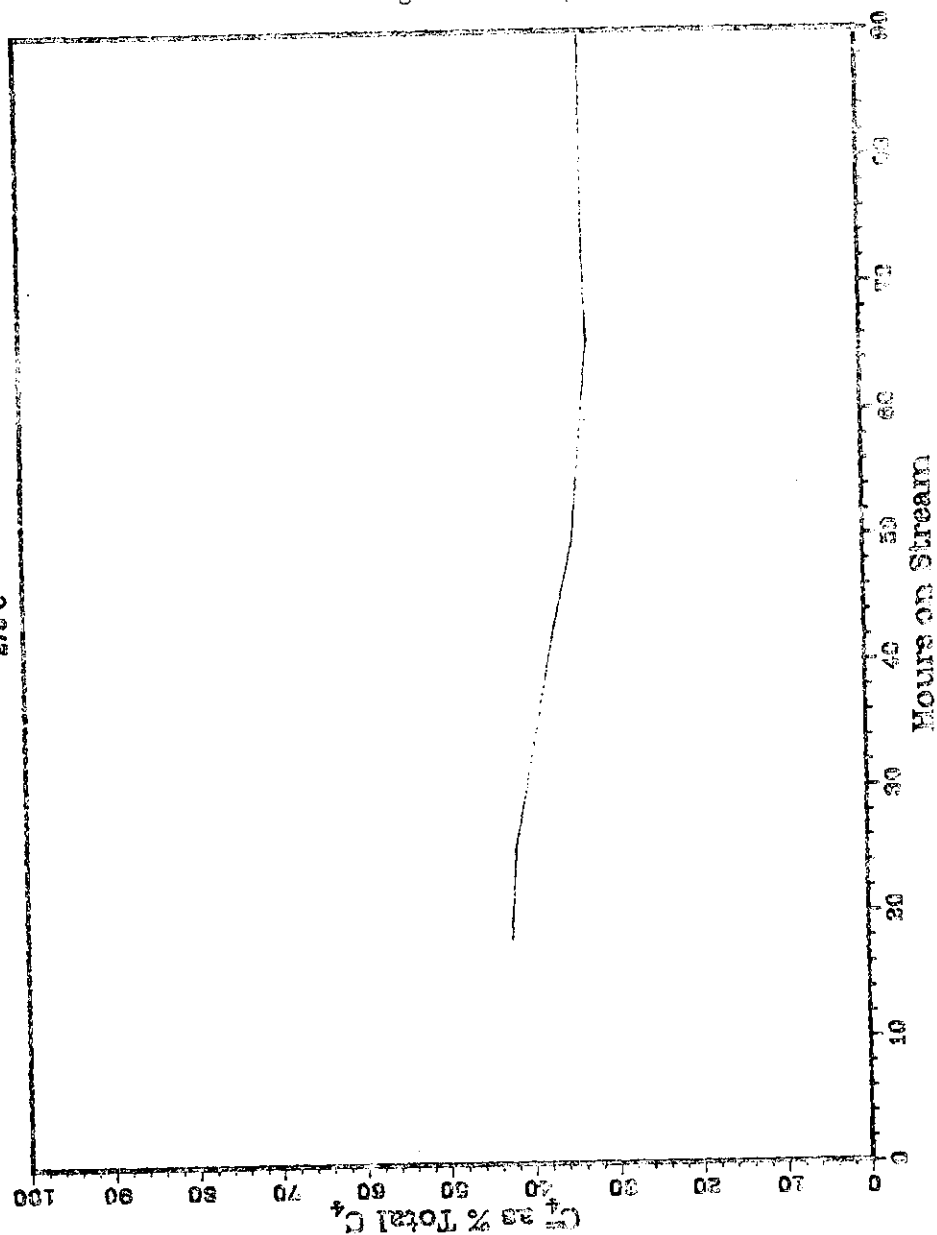


Fig. 168

Fig. 169

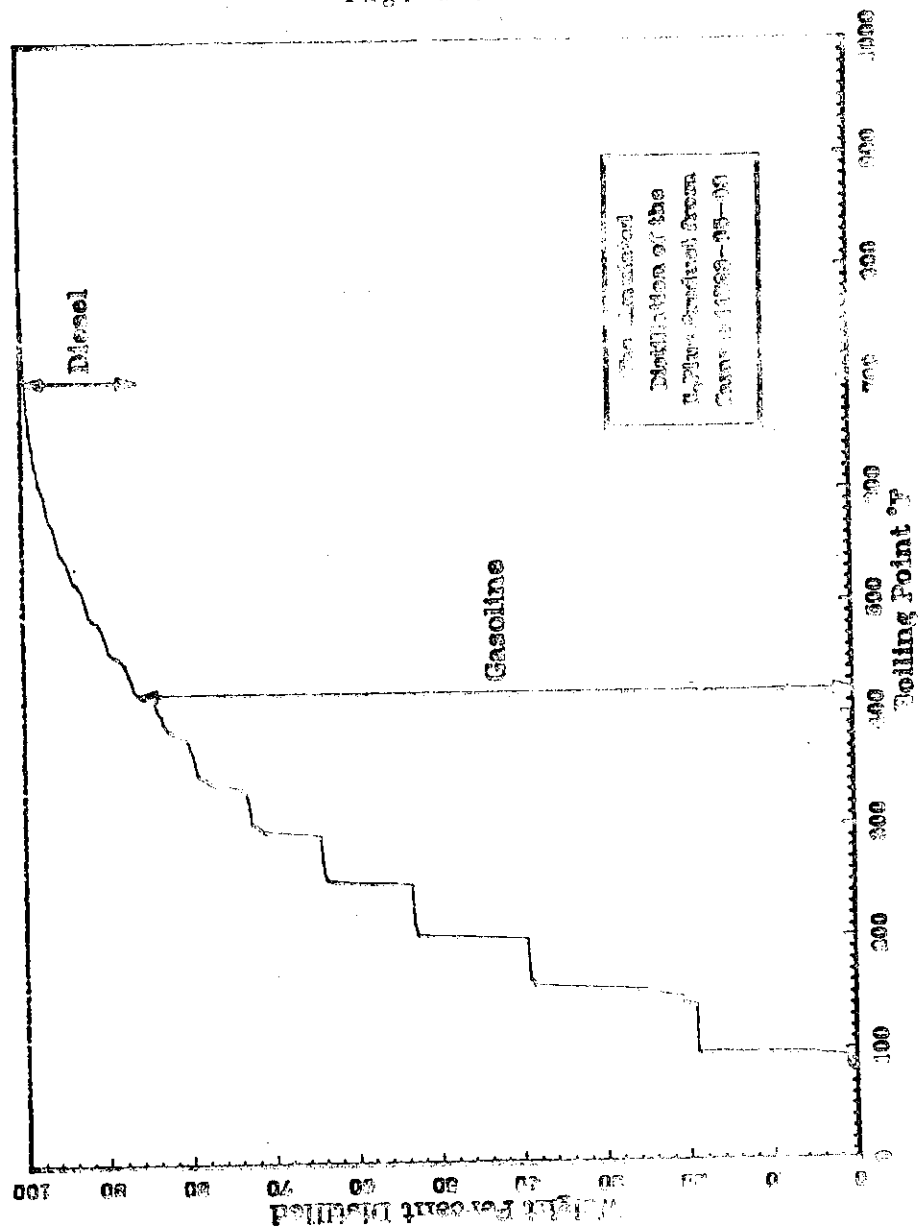


Fig. 170

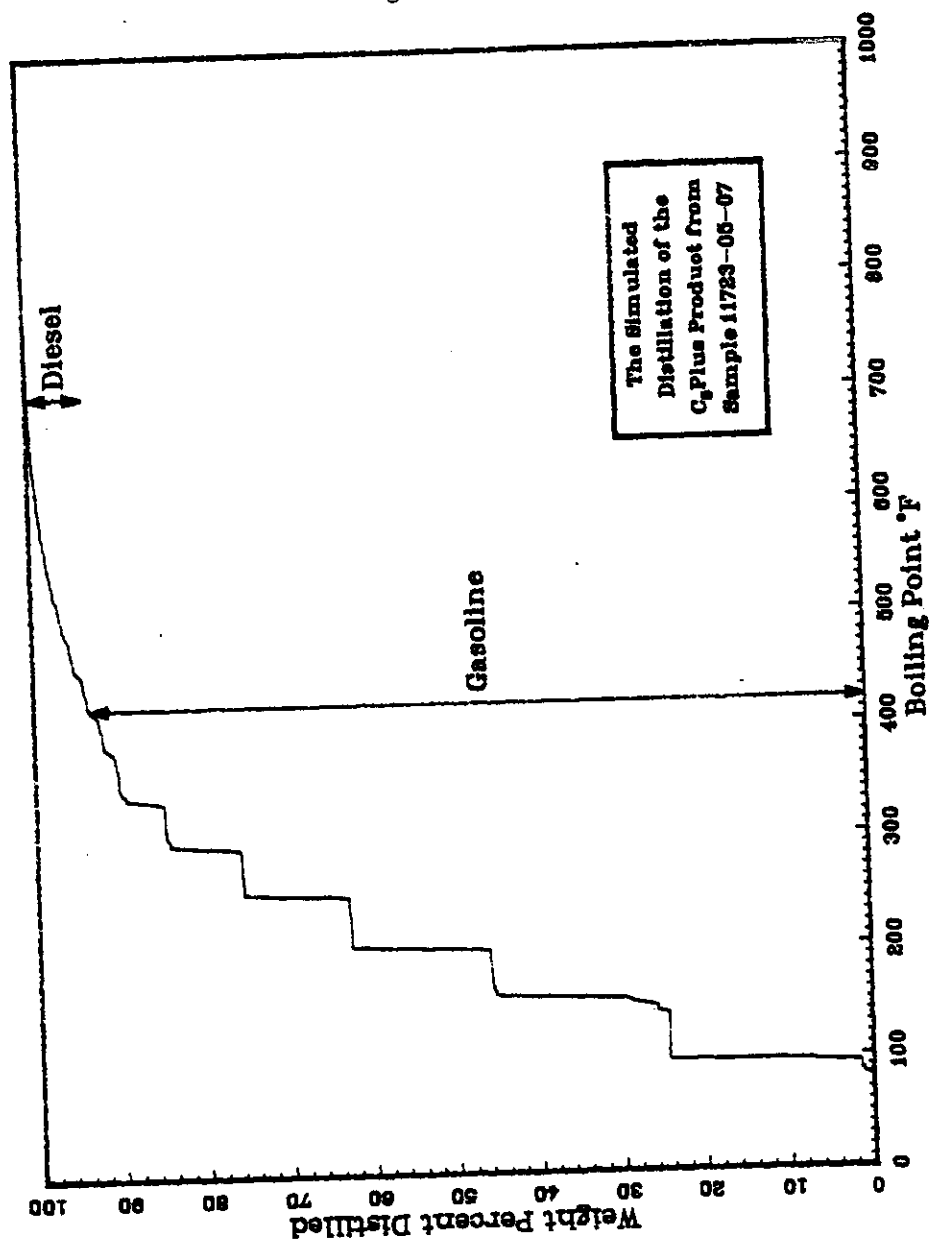


Fig. 171

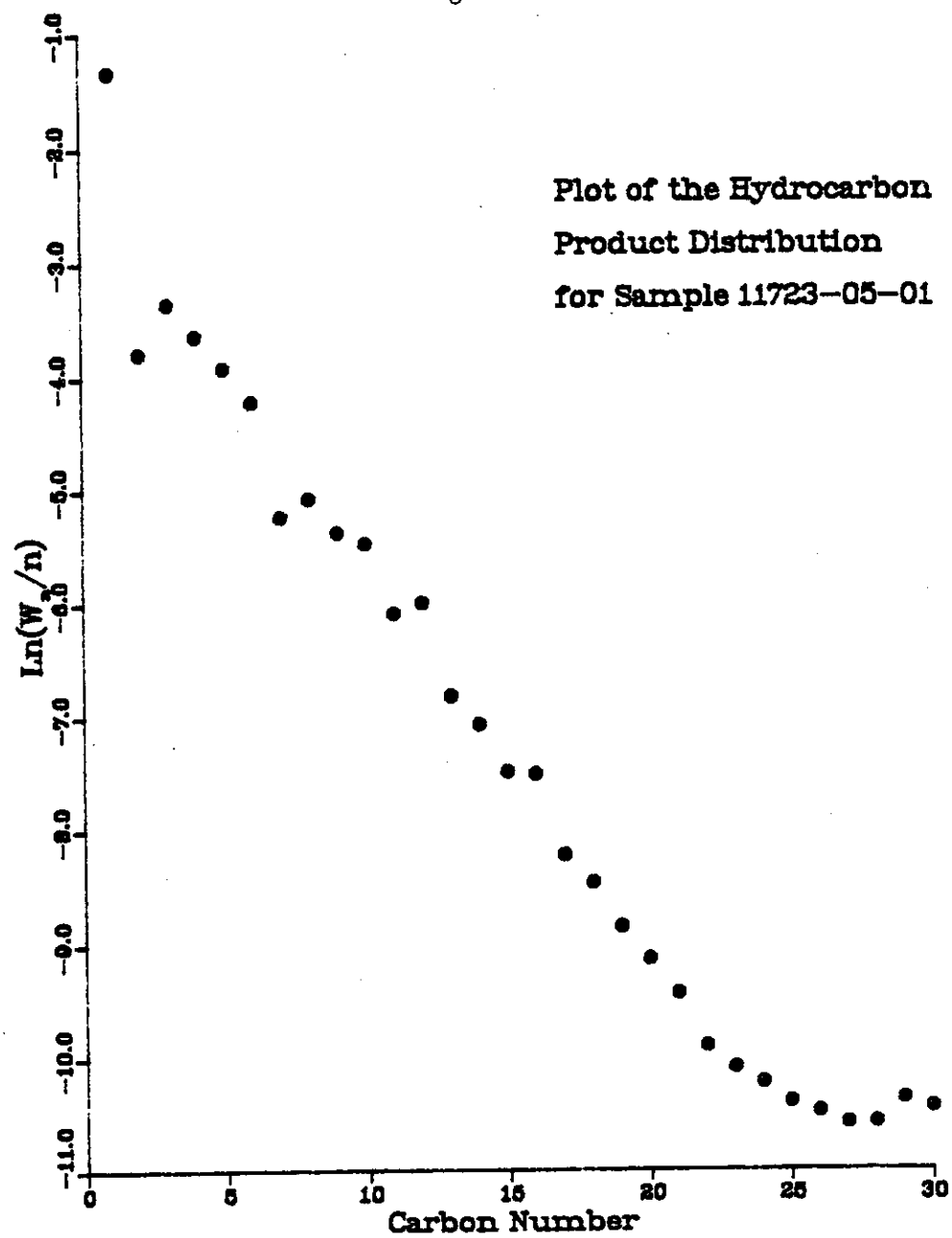


Fig. 172

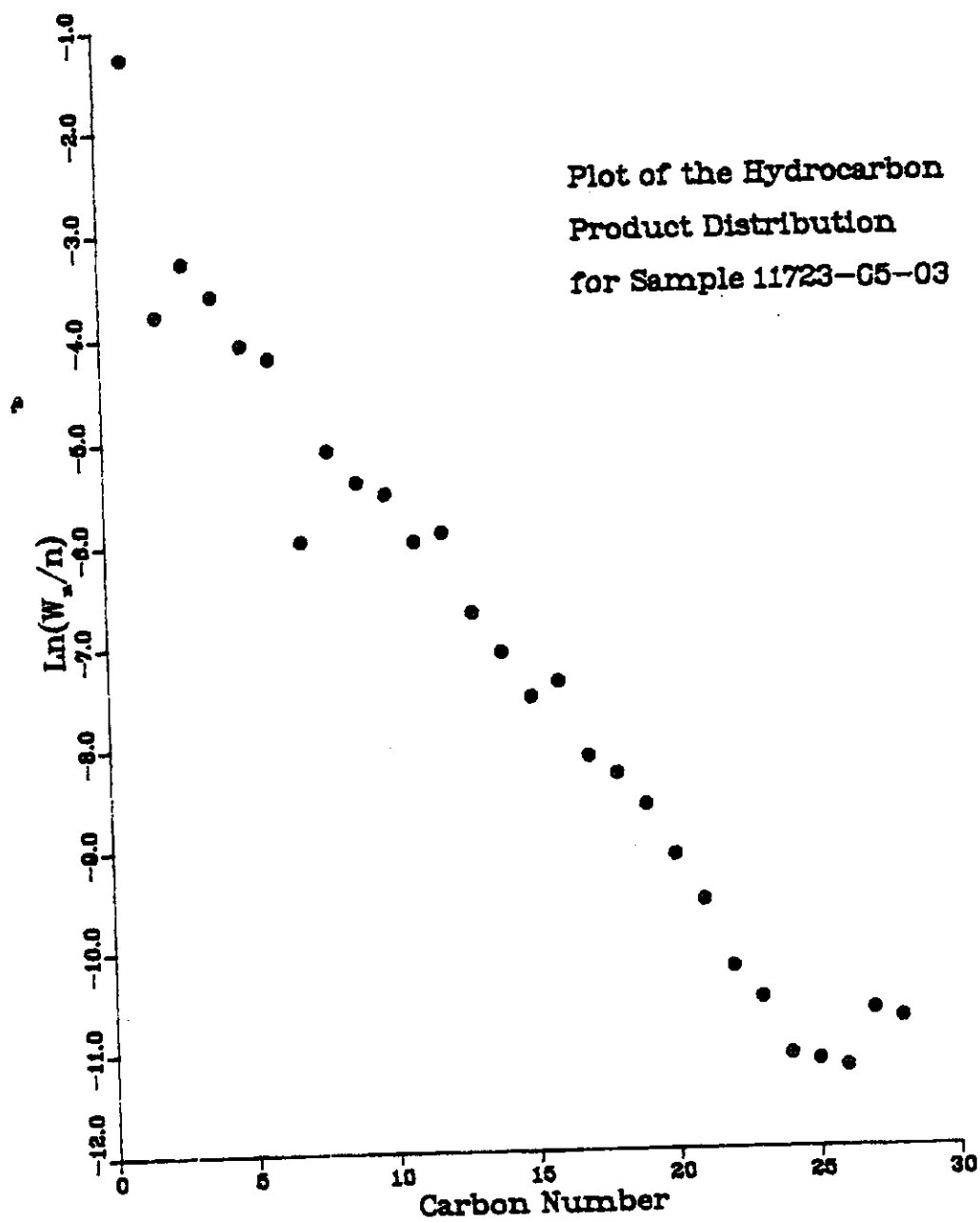


Fig. 173

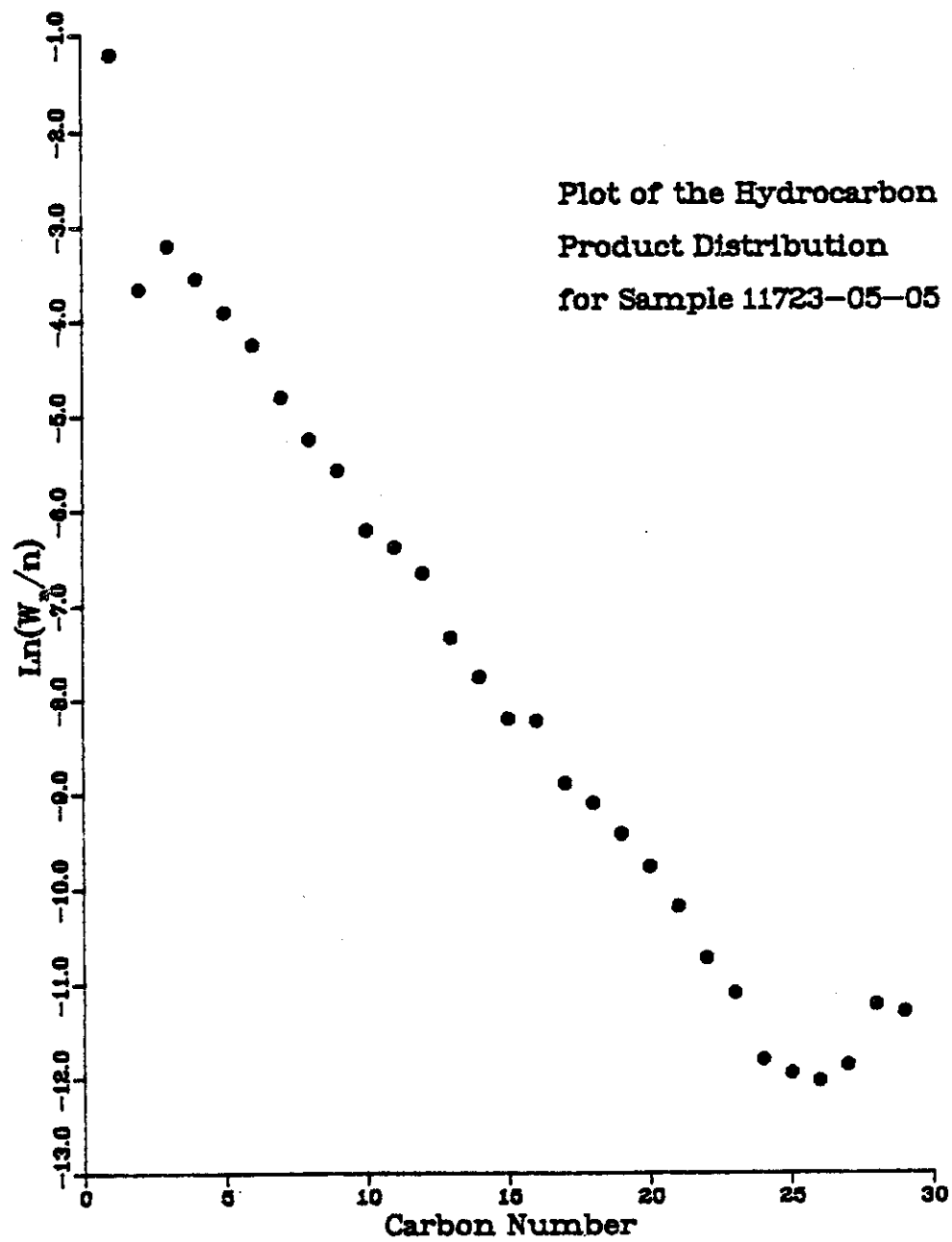


Fig. 174

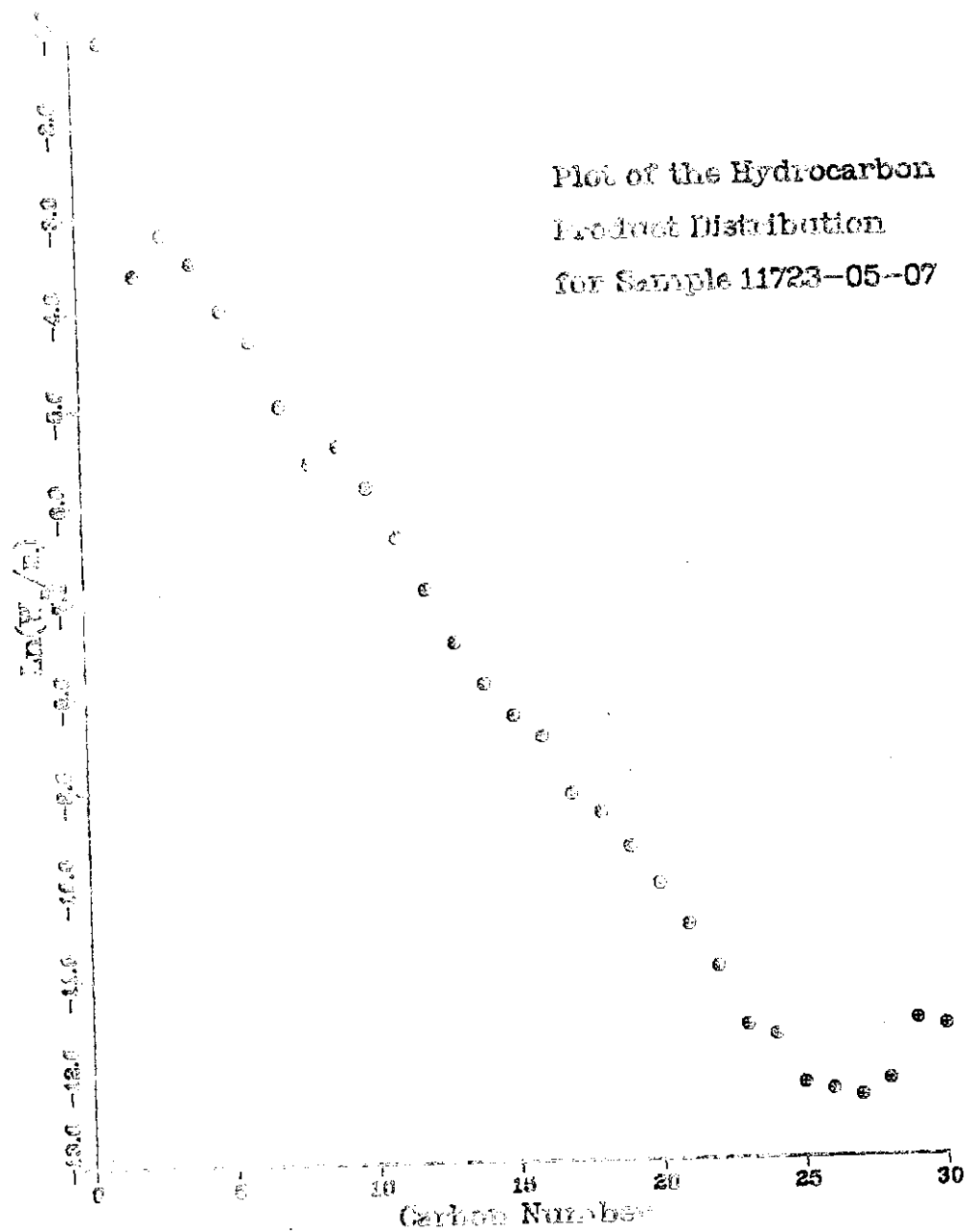


TABLE 45

RESULT OF SYNGAS OPERATION

RUN NO. 11723-05
 CATALYST CO/TH+UCC-103+UCC-101+CU/ZN-WGSC 80 CC 38.96 GM
 FEED H₂:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

	11723-05-01	723-05-02	723-05-03	723-05-04	723-05-05
	=====	=====	=====	=====	=====
FEED H ₂ :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	18.0	25.0	42.5	49.5	65.5
PRESSURE, PSIG	294	306	303	308	305
TEMP. C	271	271	271	275	272
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	18.00	7.00	24.50	7.00	23.00
EFFLNT GAS LITER	268.45	114.80	413.00	128.60	422.24
GM AQUEOUS LAYER	36.39	10.73	37.54	9.56	31.40
GM OIL	3.52	1.07	3.73	0.52	1.71
MATERIAL BALANCE					
GM ATOM CARBON %	89.19	96.13	93.49	100.06	96.77
GM ATOM HYDROGEN %	95.74	97.31	97.73	105.30	104.88
GM ATOM OXYGEN %	95.28	96.02	96.49	99.89	98.21
RATIO CHX/(H ₂ O+CO ₂)	0.7642	1.0054	0.8529	1.0093	0.9236
RATIO X IN CHX	2.6543	2.6510	2.7055	2.8075	2.7642
USAGE H ₂ /CO PRODT	2.1825	2.2194	2.2371	2.2764	2.2721
RATIO CO ₂ /(H ₂ O+CO ₂)	0.0280	0.0333	0.0251	0.0396	0.0279
K SHIFT IN EFFLNT	0.02	0.02	0.02	0.03	0.02
CONVERSION					
ON CO %	22.92	22.16	19.16	19.93	18.46
ON H ₂ %	53.54	48.45	44.44	42.91	40.26
ON CO+H ₂ %	38.78	35.38	32.08	31.71	29.80
PRDT SELECTIVITY, WT %					
CH ₄	26.45	25.54	28.24	32.13	30.29
C ₂ HC'S	4.52	4.62	4.59	6.38	5.17
C ₃ H ₈	7.20	7.99	8.12	9.09	9.02
C ₃ H ₆ =	3.27	3.45	3.22	3.23	3.20
C ₄ H ₁₀	6.18	6.86	6.99	7.78	7.85
C ₄ H ₈ =	4.39	4.77	3.96	3.99	3.66
C ₅ H ₁₂	6.17	6.87	6.88	7.36	7.26
C ₅ H ₁₀ =	3.81	3.84	1.67	2.77	2.79
C ₆ H ₁₄	6.27	7.03	6.93	6.79	7.03
C ₆ H ₁₂ = & CYCLO'S	2.61	2.65	2.06	1.73	1.58
C ₇ + IN GAS	15.46	16.20	15.32	13.48	16.28
LIQ HC'S	13.67	10.19	12.02	5.28	5.87
TOTAL	100.00	100.00	100.00	100.00	100.00

SUB-GROUPING					
C1 -C4	52.01	53.23	55.12	62.59	59.19
C5 -420 F	41.63	41.47	38.63	34.58	37.67
420-700 F	5.79	5.07	5.98	2.69	2.99
700-END PT	0.57	0.23	0.27	0.13	0.15
C5+-END PT	47.99	46.77	44.88	37.41	40.81
ISO/NORMAL MOLE RATIO					
C4	0.0596	0.0566	0.0653	0.0523	0.0660
C5	0.0758	0.0713	0.0624	0.0685	0.0575
C6	0.1464	0.1358	0.1120	0.1217	0.1061
C4=	0.0511	0.0521	0.0613	0.0615	0.0716
PARAFFIN/OLEFIN RATIO					
C3	2.1006	2.2124	2.4031	2.6875	2.6870
C4	1.3565	1.3902	1.7044	1.8848	2.0704
C5	1.5739	1.7393	3.9978	2.5877	2.5273
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.7477		0.7228		0.7015
RATIO CH4/(1-)**2	4.1550		3.6744		3.4005
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY		CLDY LT BL		
DENSITY	0.743		0.720		0.722
N, REFRACTIVE INDEX	1.4246		1.4247		1.4256
SIMULT'D DISTILATN					
10 WT % @ DEG F	300		305		328
16	311		342		345
50	416		425		431
84	548		554		554
90	601		598		599
RANGE(16-84 %)	237		212		209
WT % @ 420 F	53.50	48.00	48.00	46.50	46.50
WT % @ 700 F	95.86	97.74	97.74	97.49	97.49

TABLE 46

RESULT OF SYNGAS OPERATION

RUN NO. 11723-05
 CATALYST CO/TH+UCC-103+UCC-101+CU/ZN-WGSC 80 CC 38.96 GM
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

11723-05-06 723-05-07

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FEED H2:CO:AR	50:50: 0	50:50: 0
HRS ON STREAM	72.5	89.6
PRESSURE, PSIG	300	297
TEMP. C	273	273

FEED CC/MIN	400	400
HOURS FEEDING	7.00	24.08
EFFLNT GAS LITER	129.66	453.21
GM AQUEOUS LAYER	8.08	27.80
GM OIL	0.37	1.28

MATERIAL BALANCE		
GM ATOM CARBON %	95.36	95.83
GM ATOM HYDROGEN %	102.74	104.12
GM ATOM OXYGEN %	95.76	96.55
RATIO CHX/(H2O+CO2)	0.9756	0.9562
RATIO X IN CHX	2.8096	2.7974
USAGE H2/CO PRODT	2.2979	2.2932
RATIO CO2/(H2O+CO2)	0.0305	0.0287
K SHIFT IN EFFLNT	0.03	0.02

CONVERSION		
ON CO %	17.31	16.88
ON H2 %	37.37	36.43
ON CO+H2 %	27.72	27.06

PRDT SELECTIVITY, WT %		
CH4	32.16	31.74
C2 HC'S	5.81	5.46
C3H8	8.97	9.26
C3H6=	3.32	3.27
C4H10	8.06	8.34
C4H8=	3.81	3.97
C5H12	7.74	6.99
C5H10=	2.86	2.28
C6H14	6.87	6.71
C6H12= & CYCLO'S	1.61	1.34
C7+ IN GAS	14.26	16.03
LIQ HC'S	4.53	4.62

TOTAL	100.00	100.00
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SUB-GROUPING		
C1 -C4	62.14	62.04
C5 -420 F	35.37	35.42
420-700 F	2.37	2.41
700-END PT	0.13	0.13
C5+-END PT	37.86	37.96
ISO/NORMAL MOLE RATIO		
C4	0.0568	0.0684
C5	0.0532	0.0605
C6	0.1089	0.0874
C4=	0.0702	0.0525
PARAFFIN/OLEFIN RATIO		
C3	2.5763	2.7006
C4	2.0394	2.0292
C5	2.6338	2.9755
SCHULZ-FLORY DISTRBTN		
ALPHA (EXP(SLOPE))		0.6983
RATIO CH4/(1-A)**2		3.4872
LIQ HC COLLECTION		
PHYS. APPEARANCE		CLR OIL
DENSITY		0.706
N, REFRACTIVE INDEX		1.4262
SIMULT'D DISTILATN		
10 WT % @ DEG F		340
16		347
50		438
84		555
90		599
RANGE(16-84 %)		208
WT % @ 420 F	45.00	45.00
WT % @ 700 F	97.22	97.22

X. Run 9 (11723-07) with Catalyst 9
(Co/Th+UCC-103+UCC-101+Cu/Zn)

This is a retest of Catalyst 8, with identical formulation and preparation.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. 175-178. Simulated distillations of the C₅⁺ product are plotted in Figs. 179-180. Carbon number product distributions are plotted in Figs. 181-183. Detailed material balances appear in Table 47.

The results did not differ greatly from those of the previous run. The conversion of syngas, initially 46 percent, dropped by one percentage point every 4.3 hours on stream. The water gas shift activity was much lower than usual for a cobalt catalyst, with only 4 percent of the oxygen rejected as CO₂ and a H₂:CO usage ratio of more than 2.1:1.

The selectivity also was poor. Methane production, initially 23 percent, increased at a rate of one percentage point every 12 hours on stream. Production of C₅⁺ hydrocarbons and motor fuels was slightly higher than with Catalyst 8. The motor fuels, again mostly gasoline, were 52 percent of the product initially, and down to less than 46 percent at 68 hours on stream.

Isomerization of the pentane was even lower than usual for

cobalt catalysts. About half of the C₄ hydrocarbons were butenes (the only result of this test which is within the normal cobalt catalyst range). The Schulz-Flory plots confirm the poor product distribution; in light of the low conversion and poor selectivity, the slight non-linearity is not significant.

Clearly, there is an anti-synergetic action of some kind between this cobalt catalyst and the copper/zinc water gas shift component, one or both acting to impair the effectiveness of the other.

RUN 11723-07

1:1 H₂:CO
290 PSIG
270°C

