

	100	100	100	100	100
SUBGROUPING					
C1 -C4	19.71	25.41	25.65	27.78	28.31
C5 -420 F	23.85	28.32	30.20	32.28	32.98
420-700 F	25.88	26.90	25.20	21.34	19.64
700-END PT	30.56	19.37	18.95	18.60	19.07
C5 -END PT	80.29	74.59	74.35	72.22	71.69
ISO/NORMAL MOLE RATIO					
C4	.1382	.1235	.1304	.1388	.1288
C5	.0903	.1661	.0955	.2054	.1727
C6	.1899	.0763	.2007	.2347	.2112
C4	.0797	.0754	.0846	.0822	.0831
PARAFFIN/OLEFIN M RATIO					
C2	.3478	.3366	.3327	.3068	.2994
C3	.1168	.1218	.1188	.1165	.1210
C4	.1425	.1454	.1525	.1500	.1435
C5	.2733	.2927	.2750	.2993	.2938
L10 HC COLLECTION					
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	WAX
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	410	397	402	387	386
16	448	424	429	411	412
50	681	602	608	611	627
84	983	889	888	901	914
90	1044	971	966	975	985
RANGE(16-84 %)	535	465	459	490	502
WT % @420 F	11.9	15.2	14.5	18.6	18.0
WT % @700 F	52.3	64.5	63.3	62.1	59.6

TABLE 8D RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
 CATALYST FE₂O₃, 1%K₂O, #9673-1LE, REFERENCE CATALYST, 80 CC 86.86 GM
 FEED H₂:CO:AR OF 50/50/0.45/45/10 & 60/30/10 @ 400CC/MIN OR 300 GHSV

RUN & SAMPLE NO.	10011-6-16	0011-6-17	0011-6-18	0011-6-19	0011-6-20
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	190.3	196.8	215.6	211.1	240.1
PRESSURE, PSIG	92	92	94	100	95
TEMP. C	281	282	280	281	281
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	16.9	6.5	18.8	5.5	19.0
EFFLNT GAS LITER	281.0	91.4	310.9	90.6	315.0
GM AQUEOUS LAYER	11.66	3.3	11.6	3.1	12.38
GM OIL & WAX	10.23	3.75	15.46	4.49	12.51
MATERIAL BALANCE					
GM ATOM CARBON %	95.83	79.46	90.85	95.74	93.18
GM ATOM HYDROGEN %	92.26	78.87	95.00	93.01	91.64
GM ATOM OXYGEN %	97.12	77.72	87.89	91.00	94.73
RATIO CHX/(H ₂ O+CO ₂)	0.9724	1.0449	1.0665	1.1092	0.9661
RATIO X IN CHX	2.1389	2.1915	2.1870	2.1897	2.1331
USAGE H ₂ /CO PRODT	0.8401	0.8564	0.8779	0.8809	0.8294
K EFFLNT SHIFT REACTN	11.79	17.1612	18.6904	14.4073	12.6493
CONVERSION %					
ON CO	79.55	83.92	85.22	81.30	79.69
ON H ₂	35.00	35.73	35.09	35.74	33.95
ON CO+H ₂	49.85	51.87	51.31	51.22	49.20
PRDT SELECTIVITY, WT %					
CH ₄	8.17	7.79	7.49	7.63	8.32
C ₂ HC'S	7.90	7.46	7.14	7.14	7.61
C ₃ H ₈	0.93	0.93	0.82	0.86	0.90
C ₃ H ₆ =	10.28	10.08	8.75	9.17	9.71
C ₄ H ₁₀	0.90	0.89	0.79	0.83	0.85
C ₄ H ₈ =	8.10	8.18	7.10	7.32	7.50
C ₅ H ₁₂	1.71	1.67	1.45	1.57	1.60
C ₅ H ₁₀ =	6.47	6.31	5.44	5.73	5.95
C ₆ H ₁₄	1.94	1.88	1.51	1.64	1.69
C ₆ H ₁₂ = & CYCLO'S	3.80	3.71	3.18	3.22	3.63
C ₇ + IN GAS	20.53	19.77	18.45	17.78	19.34
LIQ HC'S	29.26	31.34	37.88	37.11	32.90
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	36.28	35.33	32.10	32.95	34.89
C5 -420 F	41.77	39.79	41.58	39.22	43.14
420-700 F	12.09	18.39	17.58	19.00	14.93
700-END PT	9.86	6.49	8.75	8.83	7.04
C5 -END PT	63.72	64.67	67.90	67.05	65.11
ISO/NORMAL MOLE RATIO					
C4	.1366	.1425	.1482	.1304	.1536
C5	.1716	.1682	.1677	.1874	.1905
C6	.2445	.2315	.2183	.2246	.2101
C4=	.0869	.0931	.0859	.0870	.0837
PARAFFIN/OLEFIN M RATIO					
C2	.2301	.2144	.2360	.2216	.2145
C3	.0868	.0879	.0895	.0894	.0889
C4	.1068	.1051	.1074	.1089	.1091
C5	.2572	.2568	.2590	.2661	.2614
L10 HC COLLECTION					
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	WAX
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	359	363	348	363	340
16	390	400	376	392	367
50	558	565	509	527	502
84	873	734	775	775	757
90	955	795	841	844	834
RANGE(16-84 %)	483	334	399	383	390
WT % @420 F	25.0	20.6	30.5	25.0	33.2
WT % @700 F	66.3	79.3	76.9	76.2	78.6

TABLE 8E RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
 CATALYST FE₂O₃.15K₂O. #9673-1 LB. REFERENCE CATALYST. 80 CC 86.86 GM
 FEED H₂:CO:AR OF 50/50/0.45/45/10 & 60/30/10 @ 400CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-6-21	0011-6-22	0011-6-23	0011-6-24	0011-6-25
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	246.4	263.4	287.7	311.2	318.6
PRESSURE, PSIG	97	93	93	96	33
TEMP. C	281	307	309	308	310
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	5.3	17.0	24.3	23.5	7.4
EFFLNT GAS LITER	104.8	259.4	367.5	347.4	124.9
GM AQUEOUS LAYER	2.6	16.93	26.46	27.04	5.33
GM OIL & WAX	5.66	13.59	14.44	16.18	3.42
MATERIAL BALANCE					
GM ATOM CARBON %	99.33	98.49	89.97	90.24	86.24
GM ATOM HYDROGEN %	93.19	94.96	93.49	94.16	93.68
GM ATOM OXYGEN %	90.47	93.32	91.00	91.33	97.02
RATIO CHX/(H ₂ O+CO ₂)	1.2101	1.0997	0.9805	0.9799	0.7829
RATIO X IN CHX	2.1073	2.1568	2.1944	2.1858	2.2245
USAGE H ₂ /CO PRODT	0.8372	0.9655	0.9587	0.9682	0.7728
K EFFLNT SHIFT REACTN	19.36	15.07	19.12	20.46	17.89
CONVERSION %					
ON CO	82.51	89.29	91.54	92.47	83.47
ON H ₂	34.83	43.39	42.49	43.18	31.91
ON CO+H ₂	50.72	58.69	58.84	59.61	49.10
PRDT SELECTIVITY, WT %					
CH ₄	7.45	9.52	10.95	10.84	12.65
C ₂ HC'S	7.00	7.46	8.50	8.52	9.71
C ₃ H ₈	0.83	0.82	0.90	0.85	0.81
C ₃ H ₆	8.77	9.92	10.61	10.28	10.58
C ₄ H ₁₀	0.76	0.75	0.85	0.79	0.67
C ₄ H ₈	6.85	7.65	8.27	7.90	7.30
C ₅ H ₁₂	1.47	1.60	1.70	1.56	1.35
C ₅ H ₁₀	5.34	5.76	6.05	5.78	5.43
C ₆ H ₁₄	1.64	1.77	1.86	1.84	1.64
C ₆ H ₁₂ & CYCLO'S	3.30	3.37	4.02	3.67	3.65
C ₇ IN GAS	17.80	20.61	21.23	19.48	20.23
LIQ HC'S	38.80	30.77	25.06	28.49	25.97
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	31.65	36.12	40.09	39.18	41.72
C4 -420 F	40.88	43.14	44.37	45.38	42.23
420-700 F	18.70	12.92	10.55	11.51	11.81
700 END PT	8.77	7.82	4.99	3.93	4.23
C5 -END PT	68.35	63.88	59.91	60.82	58.28
ISO/NORMAL MOLE RATIO					
C4	.1392	.1353	.1417	.1511	.1467
C5	.1812	.1815	.1500	.1408	.1291
C6	.2603	.1941	.2199	.2627	.2675
C4-	.0874	.0972	.0973	.0958	.1007
PARAFFIN/OLEFIN M RATIO					
C2	.2388	.2150	.2102	.2070	.2470
C3	.0899	.0784	.0814	.0792	.0731
C4	.1070	.0951	.0990	.0967	.0891
C5	.2684	.2702	.2728	.2625	.2423
LIQ HC COLLECTION					
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	WAX
DENSITY	-	-	-	-	-
N. REACTIVE INDEX	-	-	-	-	-
SIMULATED DISTILLATION					
10 WT % @ DEG F	349	341	332	305	330
16	381	365	351	331	347
50	519	511	474	438	489
84	764	810	762	669	703
90	842	883	872	767	797
RANGE (16-84 %)	383	445	411	338	356
WT % @420 F	29.2	32.6	38.0	45.8	38.2
WT % @700 F	77.4	74.6	80.1	86.2	83.7

TABLE 8F RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
 CATALYST Fe₂O₃.1%K₂O. #9673-11E. REFERENCE CATALYST. 80 CC 86.86 GM
 FEED H₂:CO:AR OF 50/50/0, 45/45/10 & 60/30/10 @ 400CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-6-26 0011-6-27 0011-6-28 0011-6-29 0011-6-30
 =====

	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	335.7	342.7	360.5	365.5	385.4
PRESSURE, PSIG	32	33	31	31	31
TEMP. C	310	310	312	312	310
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.1	7.0	17.8	5.0	19.9
EFFLUENT GAS LITER	292.4	125.5	317.9	87.6	319.0
GM AQUEOUS LAYER	9.08	3.1	8.31	2.44	19.55
GM OIL & WAX	9.11	2.17	5.02	1.75	5.26 ^c

MATERIAL BALANCE

GM ATOM CARBON %	87.86	88.62	80.09	85.05	78.38
GM ATOM HYDROGEN %	94.51	92.15	96.03	94.75	93.41
GM ATOM OXYGEN %	93.46	98.49	90.36	91.02	86.15
RATIO CHX/(H ₂ O+CO ₂)	0.8761	0.7838	0.7726	0.8674	0.8365
RATIO X IN CHX	2.2889	2.4505	2.5887	2.5605	2.5496
USAGE H ₂ /CO PRODT	0.7896	0.7515	0.7911	0.8431	1.0184
K EFFICIENT SHIFT REACTN	19.09	18.63	28.55	23.60	12.23

CONVERSION %

ON CO	81.41	78.24	84.48	83.91	84.67
ON H ₂	31.05	30.29	29.99	33.08	38.29
ON CO+H ₂	47.84	45.86	46.02	50.02	52.00

PRDT SELECTIVITY, WT %

CH ₄	16.51	21.79	28.77	29.62	26.94
C ₂ HC'S	10.18	12.12	13.35	12.79	11.94
C ₃ H ₈	0.72	0.91	1.02	1.04	0.99
C ₃ H ₆ =	8.78	9.90	9.53	9.20	10.49
C ₄ H ₁₀	0.54	0.63	0.68	0.62	0.67
C ₄ H ₈ =	6.04	6.64	5.89	5.35	6.56
C ₅ H ₁₂	1.06	1.21	1.16	0.99	1.34
C ₅ H ₁₀ =	4.16	4.45	3.53	3.04	3.69
C ₆ H ₁₄	1.29	1.46	1.18	1.09	1.54
C ₆ H ₁₂ = & CYCLO'S	2.90	3.04	2.23	1.94	2.43
C ₇ + IN GAS	18.60	19.22	15.47	15.20	19.20
LIQ HC'S	29.23	18.64	17.21	19.12	14.20

TOTAL	100	100	100	100	100
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SUBGROUPING						
C1 -C4	42.77	51.98	59.23	58.62	57.59	
C5 -420 F	37.59	34.82	28.59	27.65	33.06	
420-700 F	13.88	9.12	8.41	9.31	6.22	
700-END PT	5.76	4.08	3.77	4.42	3.12	
C5 -END PT	57.23	48.02	40.77	41.38	42.41	
ISO/NORMAL MOLE RATIO						
C4	.1587	.1411	.1528	.1532	.2017	
C5	.1306	.1326	.1429	.1410	.1572	
C6	.2484	.2639	.2684	.2727	.3051	
C4=	.1094	.1067	.1189	.1238	.1530	
PARAFFIN/OLEFIN M RATIO						
C2	.2775	.2935	.3561	.3420	.3456	
C3	.0785	.0875	.1019	.1074	.0898	
C4	.0864	.0914	.1107	.1118	.0993	
C5	.2482	.2649	.3185	.3158	.3541	
LIQ HC COLLECTION						
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	WAX	
DENSITY						
N. REFRACTIVE INDEX						
SIMULATED DISTILLATION						
10 WT % @ DEG F	339	352	349	355	336	
16	366	381	380	382	363	
50	501	514	514	521	494	
84	741	764	765	779	773	
90	836	854	860	877	875	
RANGE(16-84 %)	375	383	385	397	410	
WT % @420 F	32.8	29.2	29.2	28.2	34.2	
WT % @700 F	80.3	78.1	78.1	76.9	78.0	

TABLE 8G° RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
 CATALYST FE2O3.1%K2O, #9673-11E, REFERENCE CATALYST, 80 CC 86.86 GM
 FEED H2:CO:AR OF 50/50 0.45/45/10 & 60/30/10 @ 400CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-6-31	0011-6-32	0011-6-33	0011-6-34	0011-6-35
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	390.6	407.9	413.9	431.1	438.1
PRESSURE, PSIG	30	31	32	32	33
TEMP. C	310	310	311	310	341
FEED CC/MIN	400	400	400	400	400
HOURS FREDING	5.2	17.3	6.0	17.2	7.0
EFFLNT GAS LITER	83.8	277.9	96.5	278.8	118.4
GM AQUEOUS LAYER	4.87	17.47	6.06	16.87	5.98
GM OIL & WAX	1.94	2.52	1.01	4.58	0.43
MATERIAL BALANCE					
GM ATOM CARBON %	76.32	83.08	82.02	84.18	83.59
GM ATOM HYDROGEN %	95.12	93.15	92.18	92.56	93.15
GM ATOM OXYGEN %	78.34	92.23	91.18	91.89	92.63
RATIO CHX/(H2O+CO2)	0.9552	0.8120	0.8085	0.8351	0.8012
RATIO X IN CHX	2.4919	2.5687	2.5665	2.5126	2.8275
USAGE H2/CO PRDCT	1.0674	1.0103	1.0177	1.0180	1.0420
K EFFLNT SHIFT REACTN	17.76	8.95	8.37	7.34	7.94
CONVERSION %					
ON CO	89.31	80.38	79.52	76.97	75.40
ON H2	38.81	38.70	38.53	37.75	37.78
ON CO+H2	53.27	52.03	52.19	50.82	50.32
PRDCT SELECTIVITY, WT %					
CH4	24.11	28.87	28.72	26.51	40.77
C2 HC'S	10.48	12.67	12.93	11.96	13.40
C3H8	0.87	1.08	1.09	1.04	1.57
C3H6=	8.85	11.48	11.40	10.48	10.80
C4H10	0.60	0.73	0.73	0.70	0.83
C4H8=	5.67	6.97	7.02	6.62	5.74
C5H12	1.10	1.46	1.47	1.41	1.38
C5H10=	3.35	3.92	3.87	3.80	2.27
C6H14	1.55	1.71	1.73	1.68	1.52
C6H12= & CYCLO'S	2.43	2.68	2.58	2.56	1.61
C7+ IN GAS	22.43	20.57	19.17	18.62	16.57
LIQ HC'S	18.54	7.86	9.27	14.62	3.53
TOTAL	100	100	100	100	100

SUBGROUPING					
C1-C4	50.59	61.79	61.89	57.31	77.12
C5 @420 F	37.76	33.31	31.99	34.21	24.05
420-700 F	7.96	3.50	4.47	6.29	2.58
700-END PT	3.69	1.40	1.65	2.19	0.25
C5 END PT	49.41	38.21	38.11	42.89	26.88
ISO/NORMAL MOLE RATIO					
C4	.1710	.1689	.1747	.1786	.2109
C5	.0744	.1363	.1455	.1558	.1602
C6	.3144	.2659	.3269	.3071	.4765
C4-	.1559	.1512	.1549	.1494	.2077
PARAFFIN/OLEFIN M RATIO					
C2	.3323	.3384	.3644	.3645	.5997
C3	.0939	.0895	.0914	.0949	.1391
C4	.1026	.1015	.1000	.1024	.1392
C5	.3186	.3618	.3690	.3611	.5901
LIQ HC COLLECTION					
PHYS. APPEARANCE	WAX	WAX	WAX	WAX	OIL
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	335	335	340	321	NO
16	359	359	368	341	
50	472	467	480	450	LIQ-
84	751	722	722	687	
90	857	815	814	789	UID
RANGE(16-84 %)	392	363	354	346	
WT % @420 F	37.2	37.7	34.9	42.0	
WT % @700 F	80.1	82.2	82.2	85.0	

TABLE 8H RESULT OF SYNGAS OPERATION

RUN NO. 10011-6
 CATALYST FE₂O₃, 1% K₂O, #9673-11F, REFERENCE CATALYST, 80 CC 86.86 GM
 FEED H₂:CO:AR OF 50/50/0, 45/45/10 & 60/30/10 @ 400CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-6-36

FEED H₂:CO:AR 60:30:10
 HRS ON STREAM 455.5
 PRESSURE, PSIG 36
 TEMP. C 342

FEED CC/MIN 400
 HOURS FEEDING 17.4
 EFFLNT GAS LITER 300.9
 GM AQUEOUS LAYER 12.57
 GM OIL & WAX 3.97

MATERIAL BALANCE

GM ATOM CARBON % 85.79
 GM ATOM HYDROGEN % 94.06
 GM ATOM OXYGEN % 92.16
 RATIO CHX/(H₂O+CO₂) 0.8503
 RATIO X IN CHX 2.7443
 USAGE H₂/CO PRODT 1.0177
 K EFFLNT SHIFT REACTN 7.90

CONVERSION %

ON CO 72.20
 ON H₂ 35.23
 ON CO+H₂ 47.55

PRDT SELECTIVITY, WT %

CH₄ 37.33
 C₂ HC'S 12.54
 C₃H₈ 1.57
 C₃H₆= 9.47
 C₄H₁₀ 0.86
 C₄H₈= 5.13
 C₅H₁₂ 1.31
 C₅H₁₀- 2.03
 C₆H₁₄ 1.50
 C₆H₁₂- & CYCLO'S 1.63
 C₇+ IN GAS 13.34
 LIQ HC'S 13.30

TOTAL 1.00

SUBGROUPING		
C1 C4		66.89
C5 -420 F		23.63
420-700 F		6.20
700-END PT		3.29
C5 -END PT		33.11
ISO/NORMAL MOLE RATIO		
C4		.2158
C5		.1935
C6		.5018
C4-		.1978
PARAFFIN/OLEFIN M RATIO		
C2		.6789
C3		.1584
C4		.1611
C5		.6266
LIQ HC COLLECTION		
PHYS. APPEARANCE		OIL
DENSITY		
N. REFRACTIVE INDEX		
SIMULATED DISTILLATION		
10 WT % @ DEG F		360
16		387
50		516
84		815
90		929
RANGE(16-84 %)		428
WT % @420 F		28.7
WT % @700 F		75.3

Figure 30

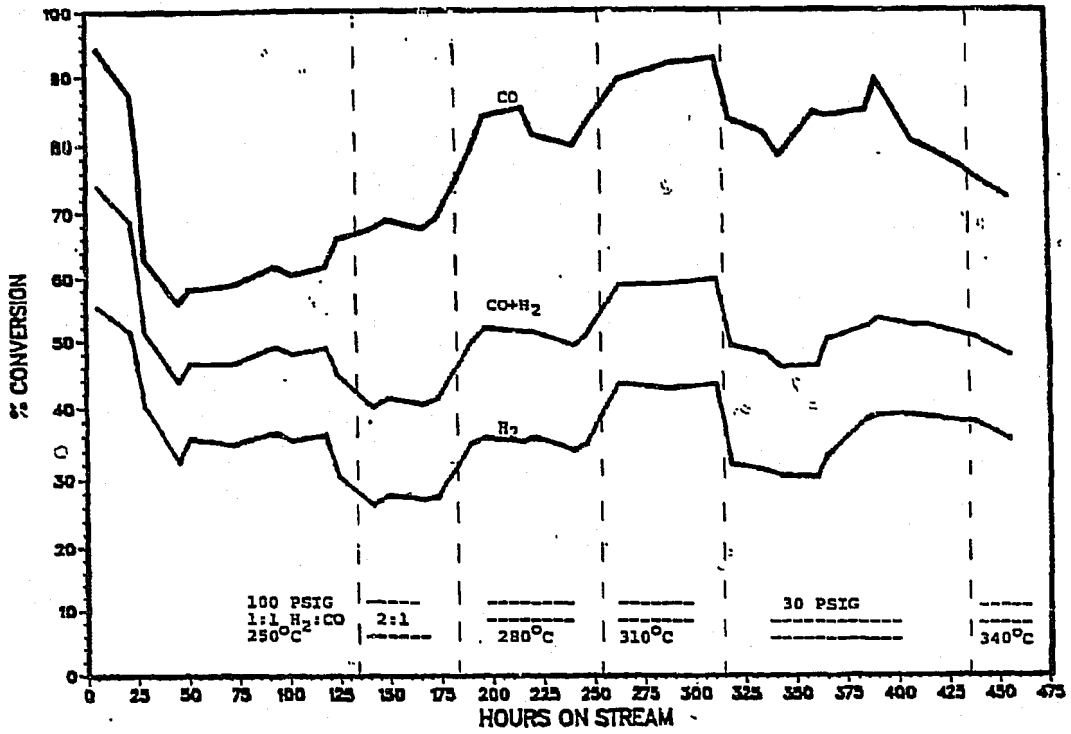


Figure 31

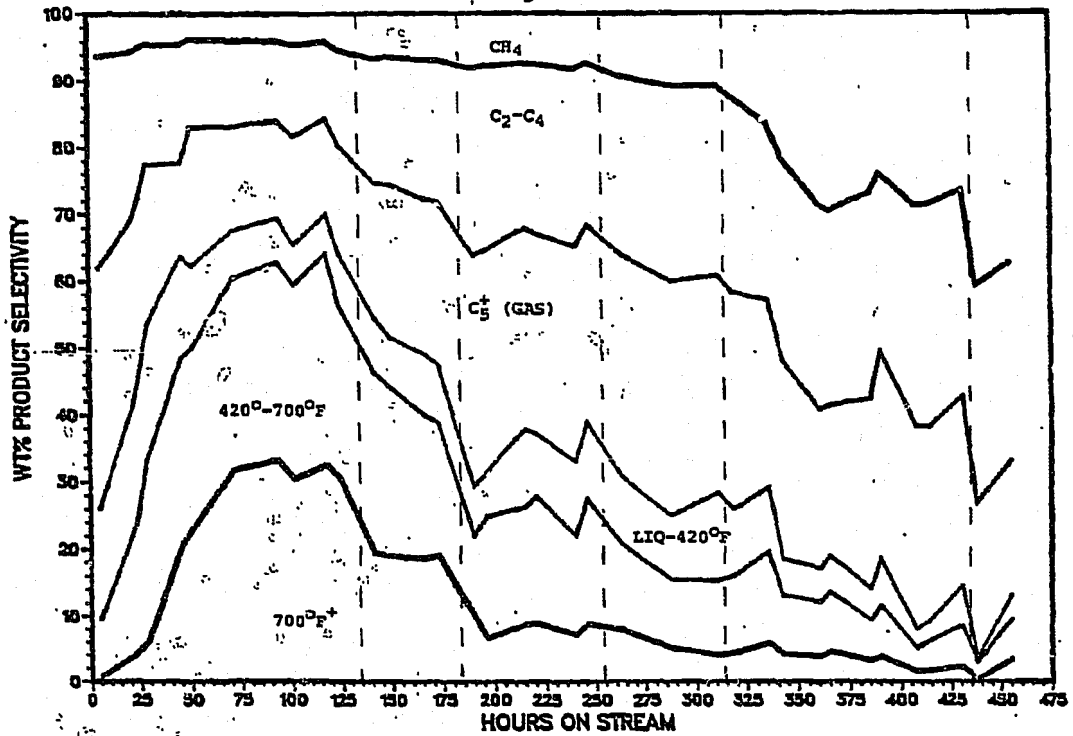


Figure 32

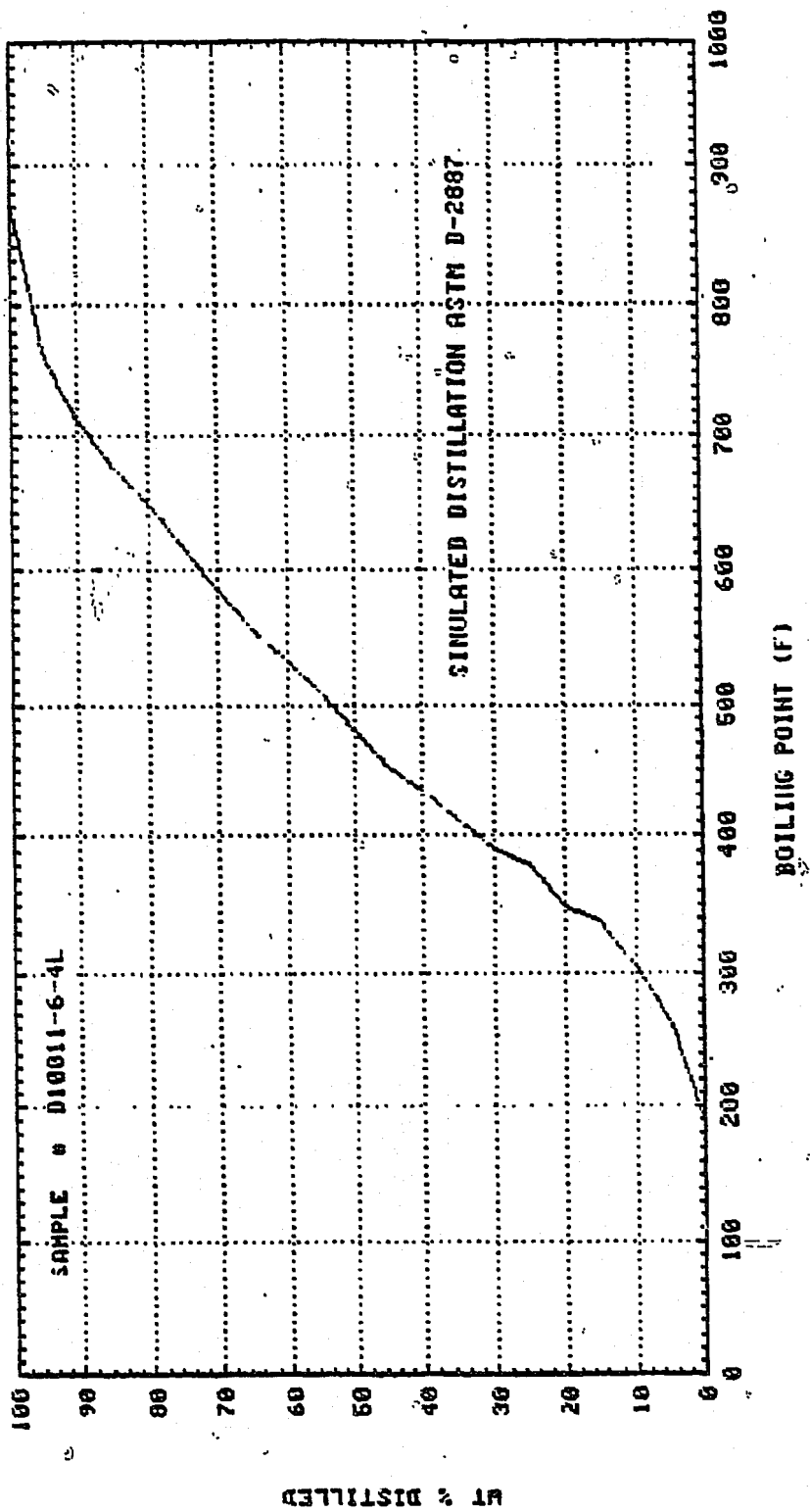


Figure 33

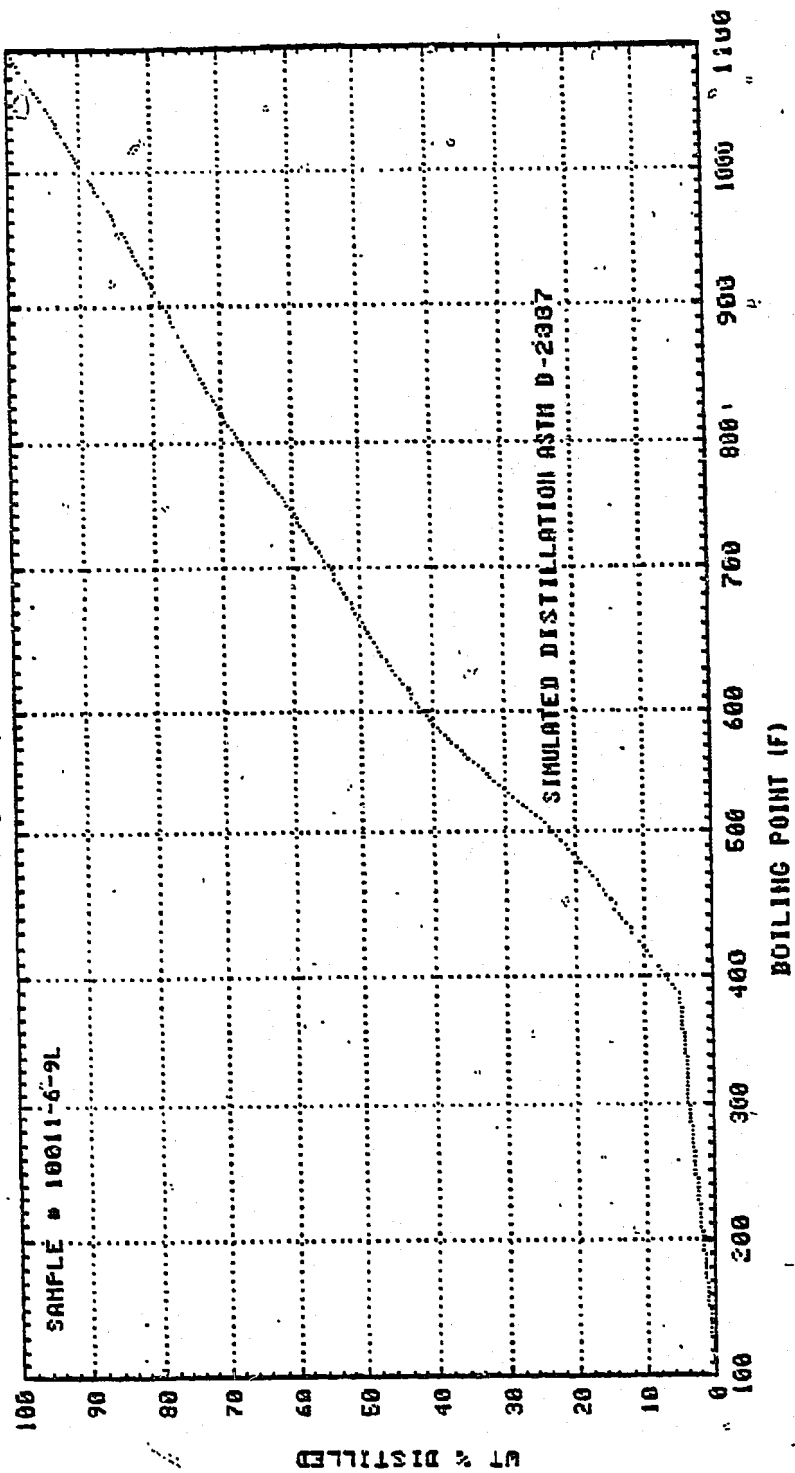


Figure 34

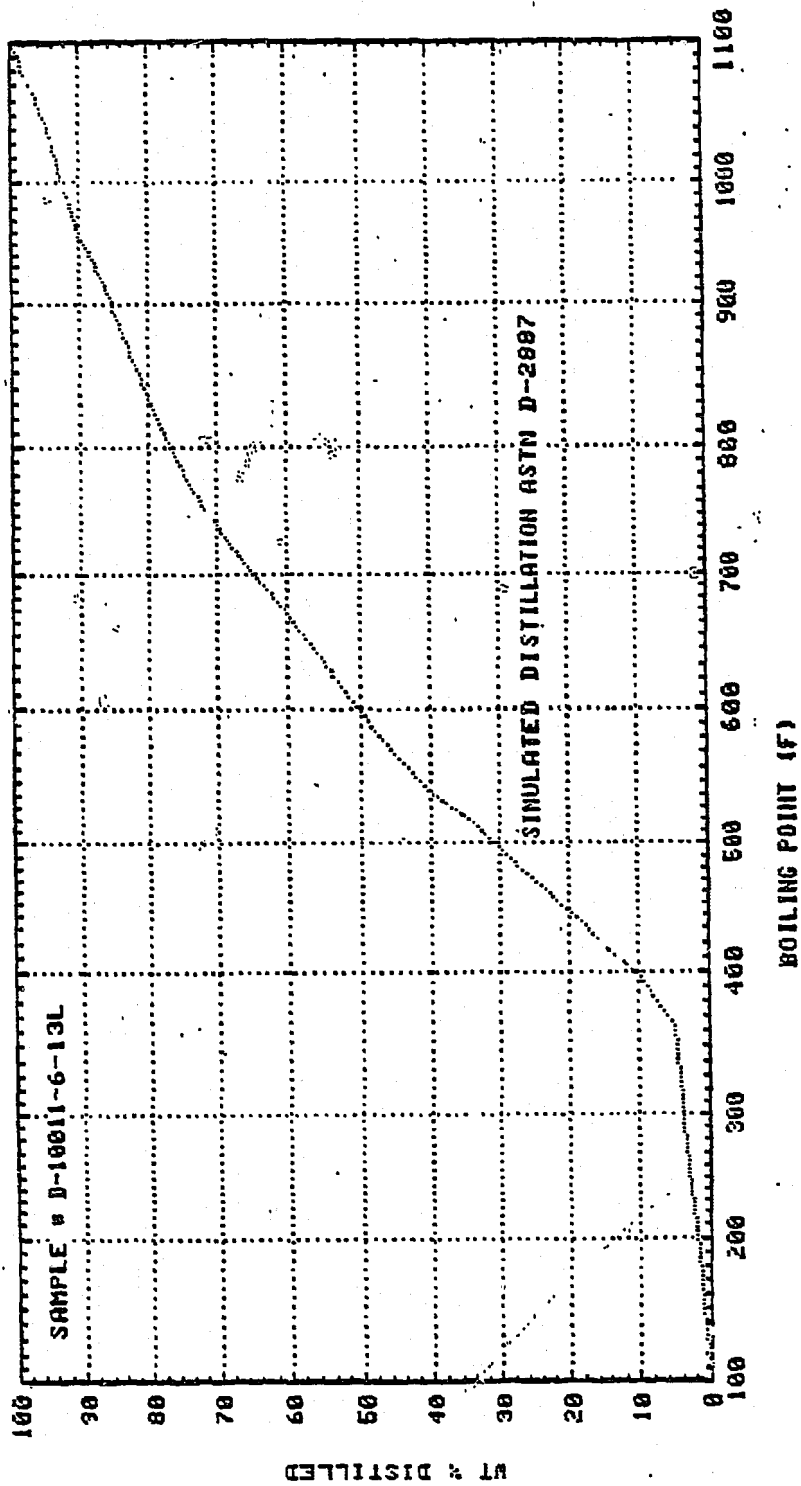


Figure 35

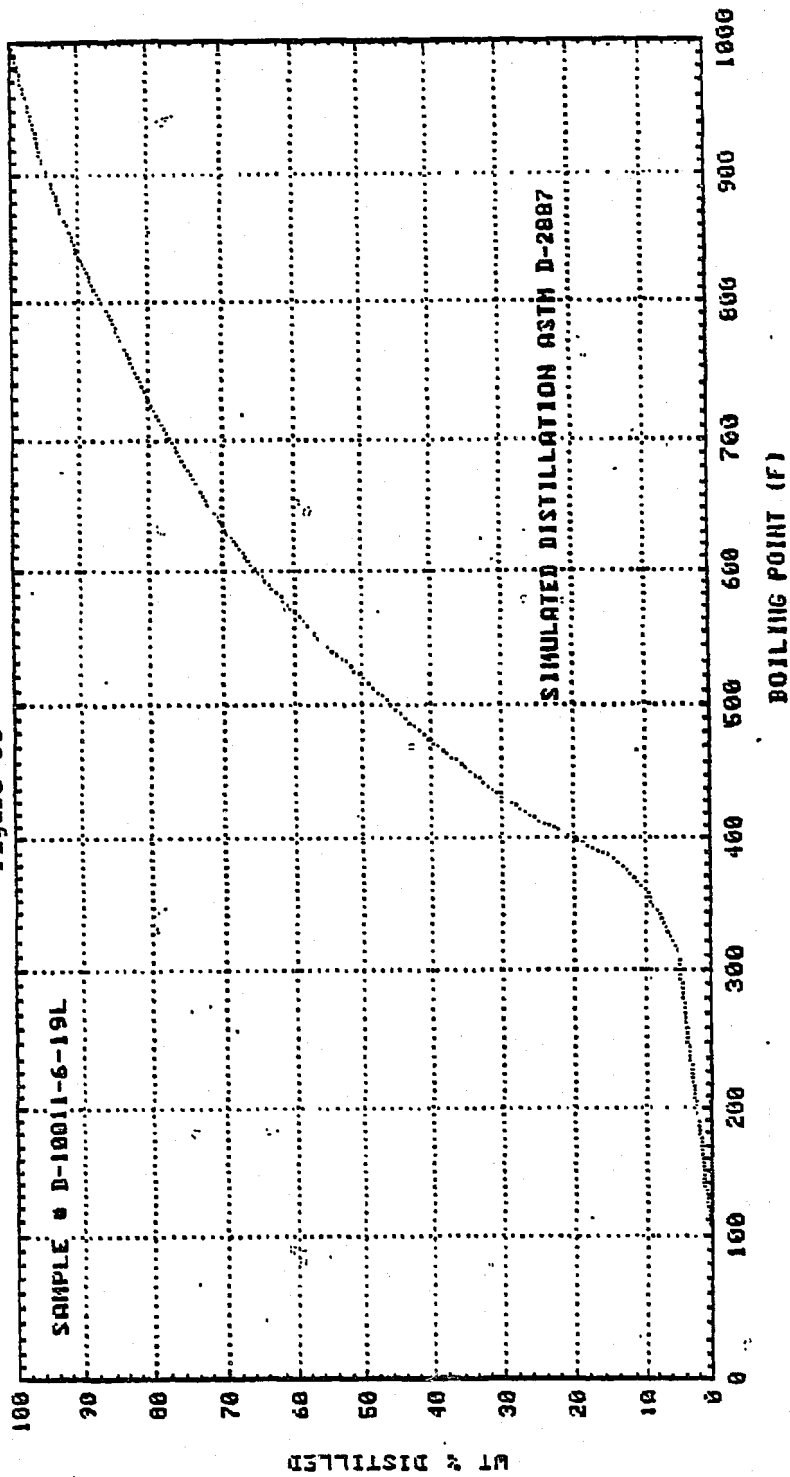


Figure 36

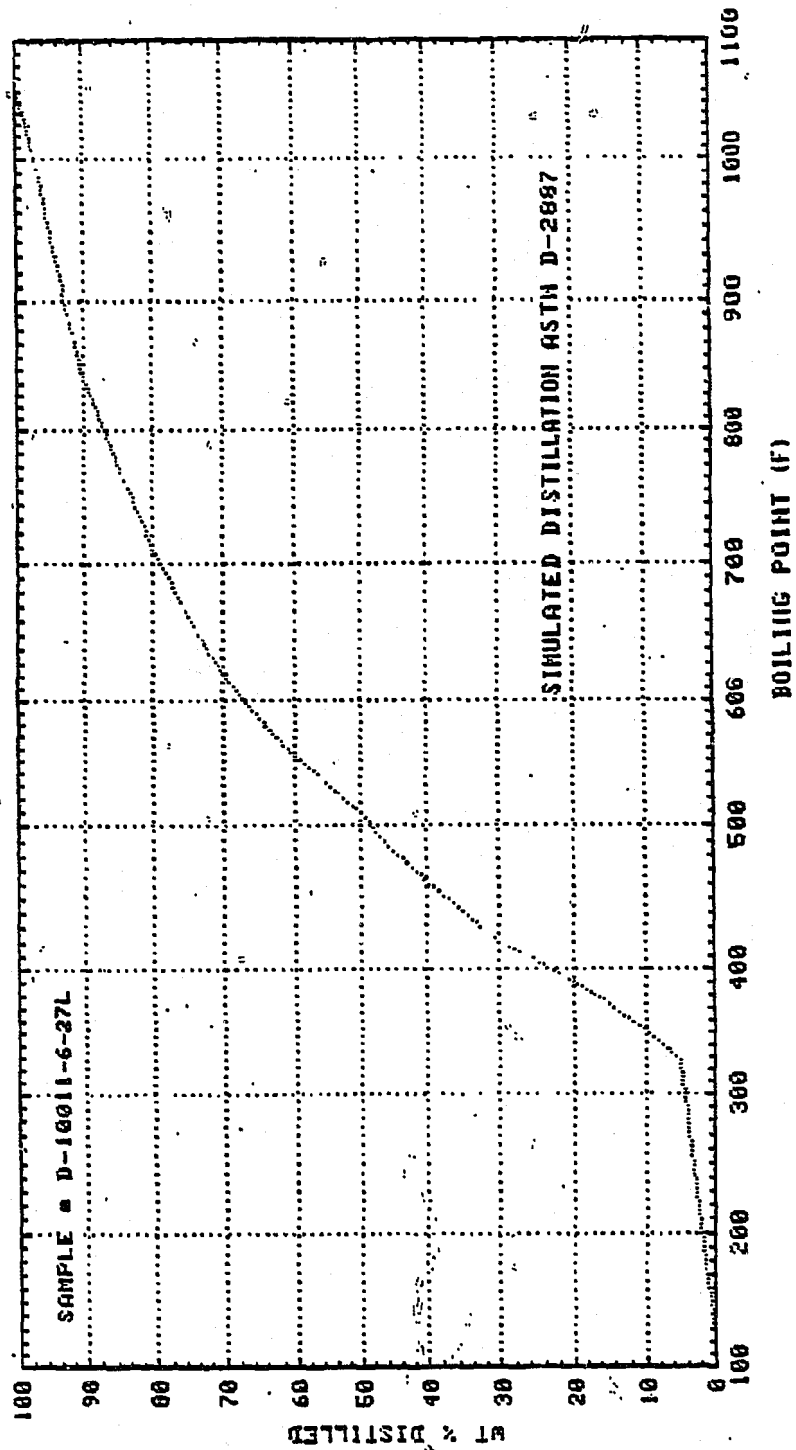


Figure 37

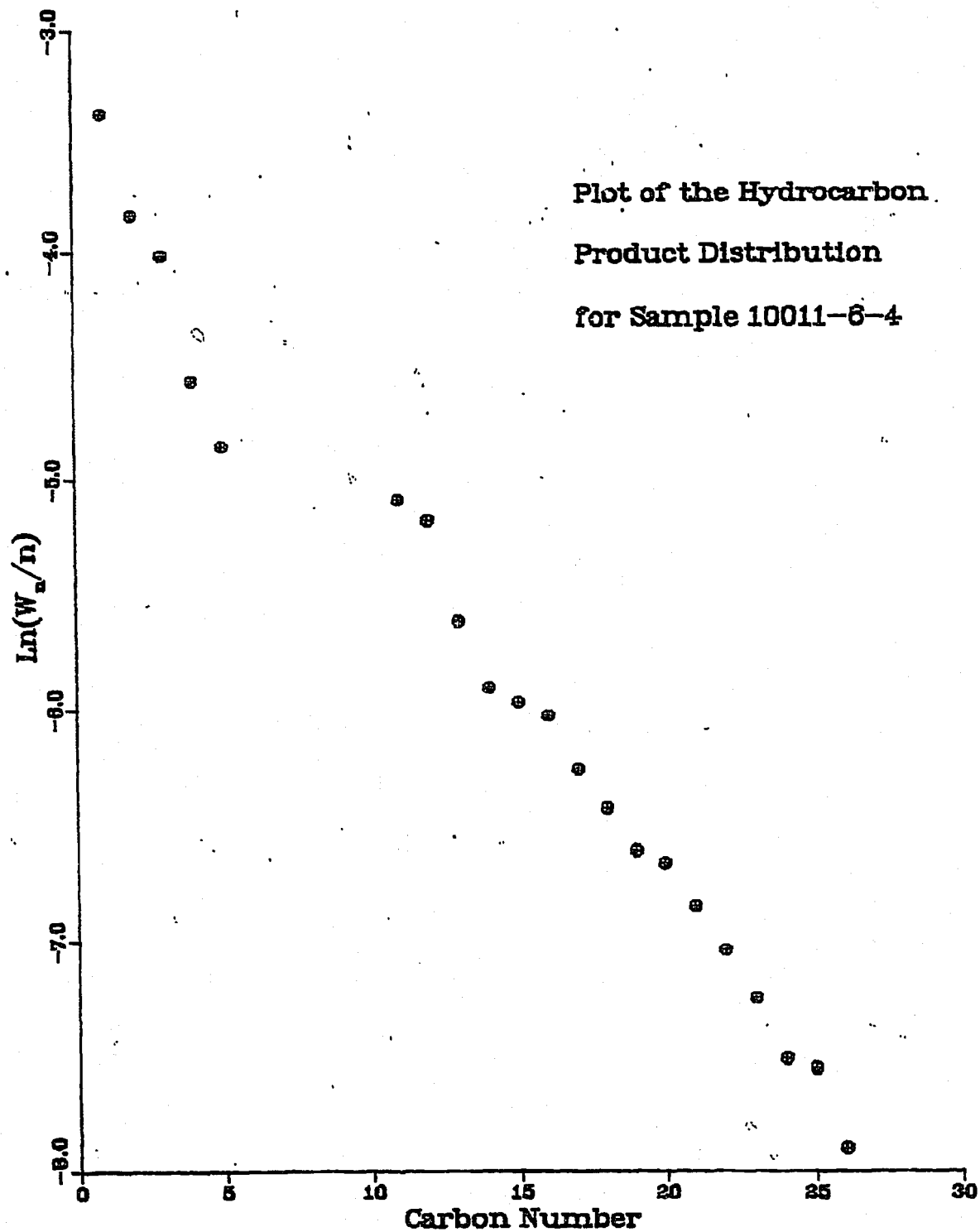


Figure 38

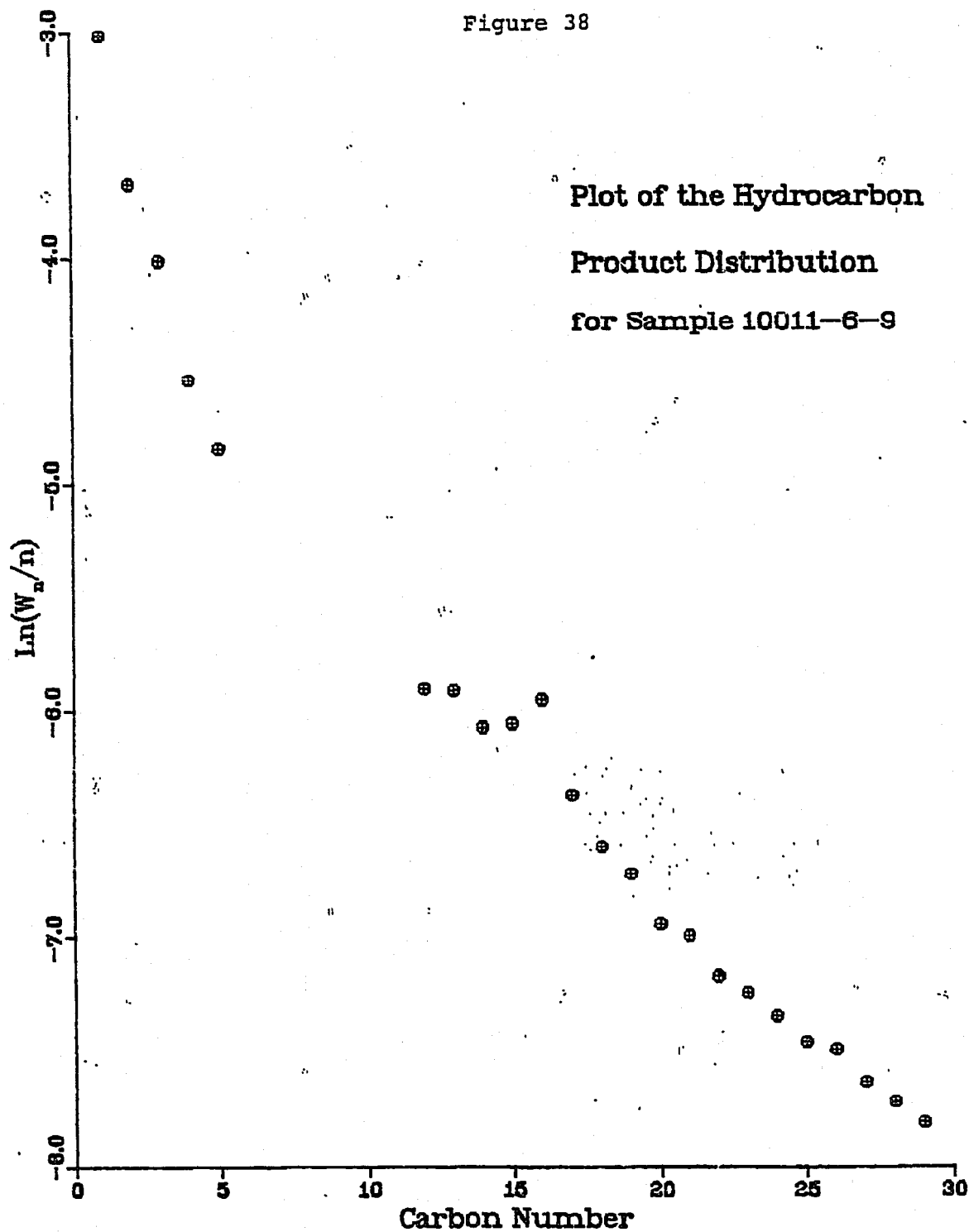


Figure 39

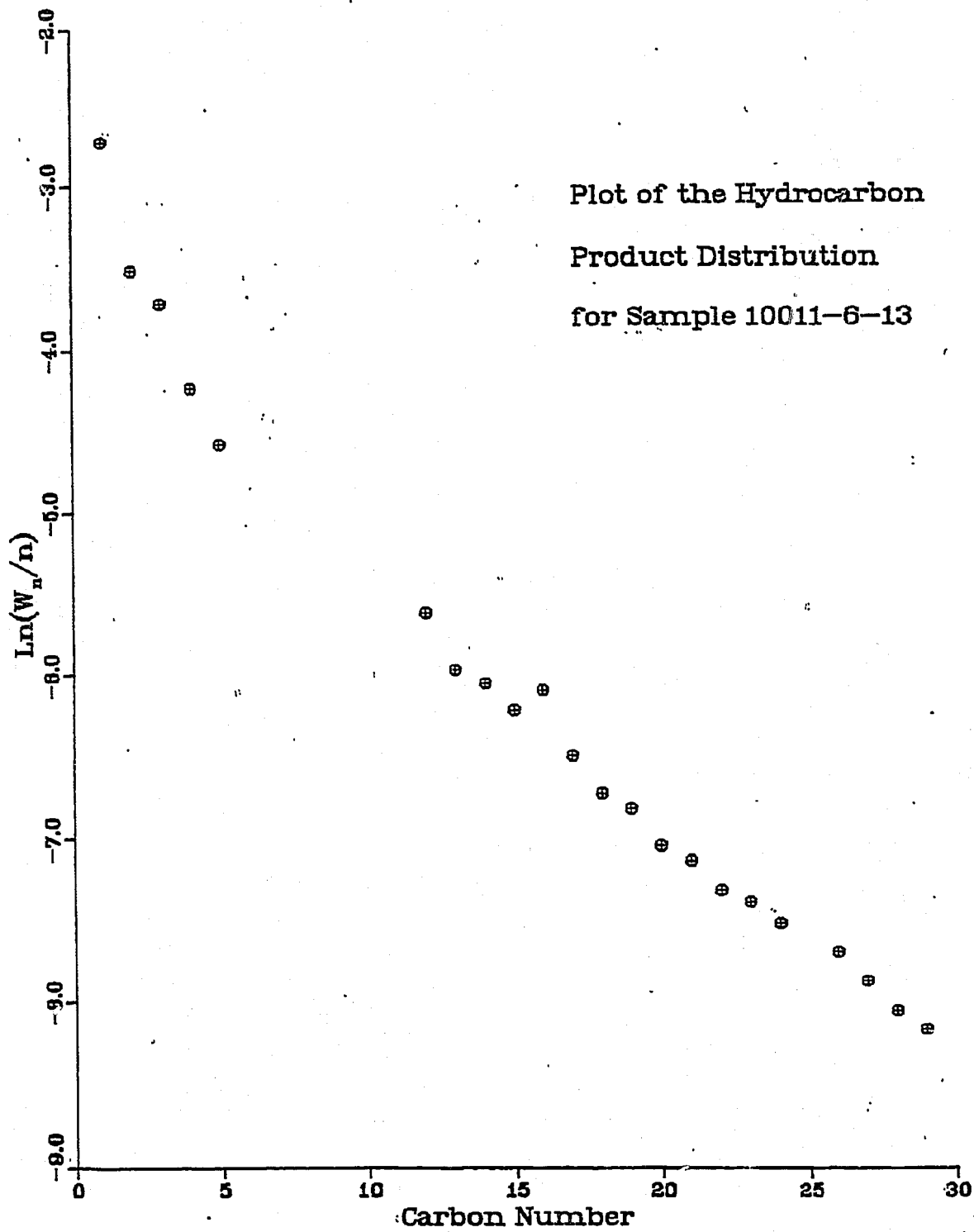


Figure 40

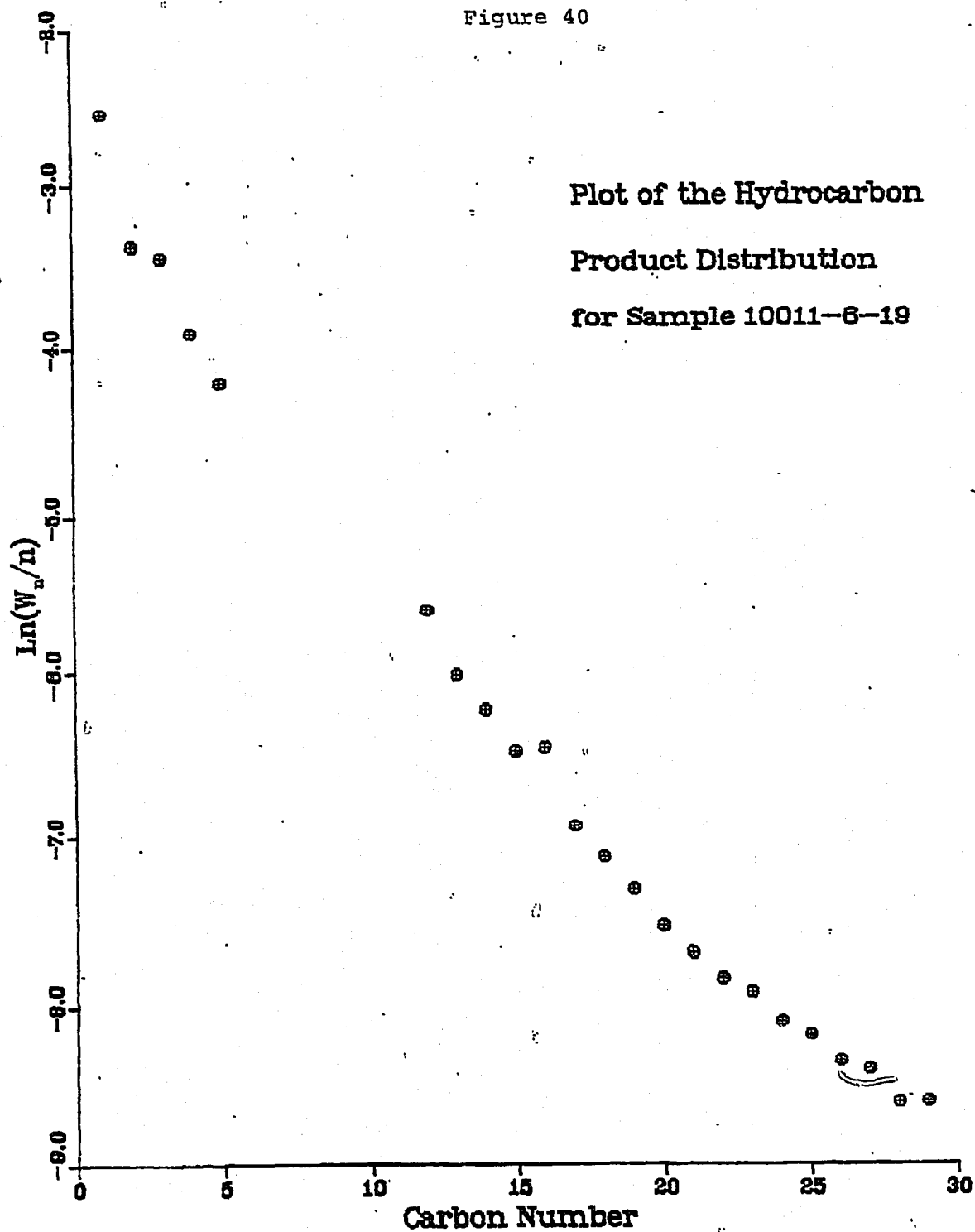
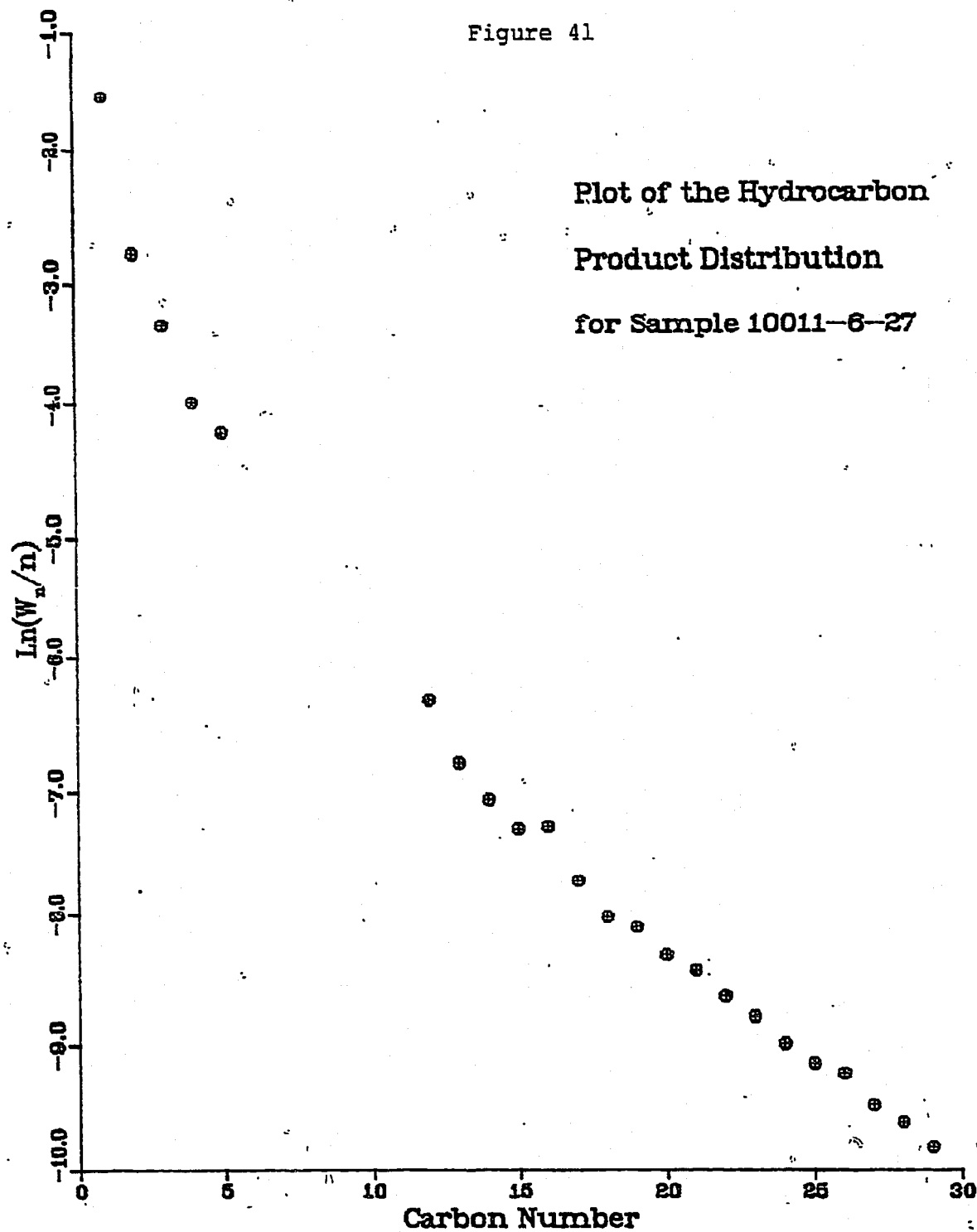


Figure 41



UCC-201 consist of a combination of iron oxide and UCC-101. It was made by pressing into pellets a powder of iron oxide precipitated on UCC-101. The iron oxide is about 50 wt% of the powder. This type of catalyst was tested several times last quarter with very disappointing results. This catalyst species was used in the first syngas shakedown run and performed quite badly giving only 5% conversion and 25% selectivity to C_5^+ . The results of the current test are far superior to those of the first run but still look inferior to the results of other catalysts reported this quarter. It must be remembered that this catalyst has almost no water gas shift activity. A large portion of the carbon in the conversion CO goes into hydrocarbon formation. In contrast with alkali-promoted catalysts, half of the carbon in converted CO goes into CO_2 formation. If the CO conversion of this catalyst is half that of an alkali-promoted catalyst, the rate of production of hydrocarbons from CO is the same. Because of the lack of water gas shift activity in the catalyst, a 2:1 $H_2:CO$ syngas was chosen as initial feedstock instead of the standard 1:1 $H_2:CO$ syngas used with promoted catalysts.

The results of the testing are presented in Tables 9A to 9E. The conversion and hydrocarbon selectivity as a function of time on stream are presented in Figures 42 and 43. Plots of the simulated distillation of the condensed hydrocarbon products from samples representative of the first three process conditions are presented in Figures 44 to 48. Plots of the hydrocarbon product distributions of these three conditions, graphed in a Schultz-Flory format are given in Figures 49 to 51.

The process conditions investigated during this run were not nearly as varied as during the immediately prior run. The initial reactor temperature and pressure were the same as in the previous run. Following the start, the pressure was increased to 300 to increase the syngas conversion. This condition, 300 250°C, with a 2:1 $H_2:CO$ syngas feed was the same used in the first run, 9710-18 where the conversion was only 5%. This time the catalyst was much more active.

After five days the temperature was increased from 250 to 280°C. This change was again to increase the conversion. After seven days on stream the feed was changed from 2:1 syngas to 1:1 syngas. The purpose of this change was to improve the product selectivity. Lowering the hydrogen in the feed lowers the hydrogen in the products leading to heavier soiling hydrocarbons. The purpose of the final condition using 2:1 syngas at 310°C and 300 was to see the effect of the higher temperature on conversion and selectivity. Most of the data taken during this run were of good quality. During a few sampling periods sufficient condensed hydrocarbon product was produced to determine boiling point distribution of the products. Density and refractive indices were not determined for any of the products.

The conversion of the syngas was low at 250°C, averaging 20%. The H₂:CO usage ratio of 1.85 indicated the catalyst was efficiently using the 2:1 syngas since the hydrogen and carbon monoxide were converted at rates proportional to their concentrations. The usage ratio was so high because of the lack of water gas shift activity. Almost all the carbon in CO converted became hydrocarbons; less than 15% went into CO₂. At 280°C the conversion of syngas increased by 60%. The H₂:CO usage ratio dropped to 1.6. This was because the water gas shift (WGS) activity increased relative to the Fischer-Tropsch activity. Slightly over 20% of the CO converted to CO₂. This lowered the usage ratio in spite of the fact that the hydrocarbons produced became more hydrogen rich.

Switching to 1:1 syngas resulted in lower syngas conversion. The catalyst was not able to use that syngas effectively. The H₂:CO usage ratio was still 1.4 while the feed ratio was 1.0. But the feed change did change the product distribution in the desired manner. The X in CH_X dropped from 2.64 to 2.35 and the catalyst produced heavier hydrocarbons. At 310°C the W.G.S. increased so much relative to the F-T synthesis activity that the catalyst could not use the 2:1, H₂:CO ratio syngas effectively.

Besides having poor water gas shift activity, unpromoted catalysts also have poor product selectivities producing much methane and only small amounts of liquid hydrocarbons. In Run 9710-18, this catalyst produced 30% methane, and only 25% C_5^+ products, none of which was collected as liquid in our experimental operations. Under identical reaction conditions in this test the catalyst performed better than in 9710-18. It produced only 16% methane and almost 50% of the hydrocarbon product was C_5^+ , some of which was condensed and analyzed by Simulated distillation. At 280°C with the 2:1 syngas feed, 20% of the product was methane. When the feed was switched to 1:1 syngas the methane dropped to 12% of the product. This was almost down to the level seen in the promoted catalysts.

The other light hydrocarbons analyzed in the gas phase revealed other aspects of the catalyst's performance. This catalyst hydrogenated more effectively than the reference iron catalyst. This aspect is seen clearly in the C_3 and C_4 hydrocarbon contact. These hydrocarbons produced in this test had much higher paraffin: olefin ratios than the corresponding hydrocarbons produced by the reference iron catalyst. The C_4 , C_5 and C_6 paraffins, many of which were separated and identified, showed this catalyst to produce a much more isomerized product than the reference iron catalyst. This was one of the desired effects of the molecular sieve component. The switch from the 2:1 to the 1:1 syngas did not change the isomerization ability of the catalyst but did produce a much more olefinic product. The effect of this feed change on the selectivity to C_2-C_4 products was much less than that to methane. The methane dropped 45% after the switch to 1:1 syngas while the C_2-C_4 selectivity only dropped 20-30%.

The overall selectivity to C_5+ hydrocarbons was not outstanding but considering the fact that this catalyst was not promoted, the selectivity was better than expected. Under optional conditions, a catalyst which follows a Schultz-Flory product distribution would produce 51% of the hydrocarbons in the range C_5 to C_{12} , R.T. to 420°F . boiling range. At 250°C this catalyst produced 43% of the hydrocarbons in the gasoline range. At 280°C with 1:1 syngas feed the catalyst produced up to 50% of the hydrocarbons in this range. Thus, this unpromoted catalyst was almost as good at gasoline production as the theoretical best catalyst. A large difference does occur in the diesel oil range. The best gasoline catalyst would produce another 15% of the hydrocarbons in the diesel range for a total selectivity to motor fuels of 66%. However, this unpromoted catalyst produced very little diesel oil or heavier material. This selectivity to total fuels is much less than that of the "theoretical" F.T. catalyst.

Analysis of the hydrocarbon product distribution indicated only the expected minor deviations from a Schultz-Flory distribution. Each of these product distributions had only a single α value. Data for C_6 to C_{11} was unavailable because of the problems with identifying the heavy hydrocarbons in the gas analysis. Unfortunately, the missing product carbon distribution data accounted for a larger percentage of the hydrocarbons produced. There are possible major deviations from the straight line which will not be seen until correlations can be developed to estimate the distribution of products in that carbon number region. The simulated distillation plots showed the expected smooth curves starting with sample #4. The chromatograms revealed more than just the presence of unbranched hydrocarbons. This was expected from the analysis of the C_4 to C_6 hydrocarbons. Sample #2 had an unusual boiling point distribution. The first part of the liquid, 10-80 wt. %, distilled in a range of 180°F . The next 15% distilled over a 200°F . range. This was an unusually long high boiling tail. Sample #3 had a break in the smooth curves at 420°F . The reason for this high concentration of a single component, which is common in task 1 testing but not task 2, is unknown.

This catalyst had a good selectivity to gasoline. Unfortunately the non-gasoline products were mostly gases instead of heavier liquids. While the catalyst had good activity and gasoline selectivity, the selectivity to total motor fuels was poor.

TABLE 9A RESULT OF SYNGAS OPERATION

RUN NO.	10011-7				
CATALYST	UCC-201, (FE-UCC-101), #9673-11C 80 CC 62.0GM				
FEED	H2:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MIN OR 300 GHSV				
RUN & SAMPLE NO.	10011-7-1	10011-7-2	10011-7-3	10011-7-4	10011-7-5
	=====	=====	=====	=====	=====
FEED H2:CO:AR	60:30:10	50:50:0	60:30:10	60:30:10	60:30:10
HRS ON STREAM	20.7	27.5	45.8	70.0	74.6
PRSSURE, PSIG	103	198	302	307	301
TEMP. C	250	275	249	250	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	20.667	6.8	18.25	24.167	4.583
EFFLNT GAS LITER	470.2	140.8	363.5	490.1	92.0
GM AQUEOUS LAYER	1.4	4.91	14.5	19.92	4.024
GM OIL	0.0	0.59	1.16	1.39	0.226
MATERIAL BALANCE					
GM ATOM CARBON %	93.26	-	89.44	94.04	92.55
GM ATOM HYDROGEN %	90.72	-	88.01	88.31	90.49
GM ATOM OXYGEN %	93.82	-	94.61	99.14	96.65
RATIO CHX/(H2O+CO2)	0.9363	-	0.7508	0.7656	0.8189
RATIO X IN CHX	2.6653	-	2.4971	2.4804	2.4545
USAGE H2/CO PRD'T	1.6721	-	1.8738	1.8272	1.8478
K EFFLNT SHIFT REACTN	0.61	-	0.22	0.25	0.25
CONVERSION %					
ON CO	11.02	-	19.79	20.48	22.82
ON H2	9.73	-	21.59	22.56	23.65
ON CO+H2	10.17	-	20.98	21.84	23.37
PRD'T SELECTIVITY, WT %					
CH4	22.32	NO GC	16.32	16.16	15.06
C2 HC'S	9.63	.	9.69	9.88	9.34
C3H8	9.07	.	6.70	6.23	6.50
C3H6=	3.68	.	7.25	7.71	7.66
C4H10	6.65	.	4.27	3.91	3.96
C4H8=	4.53	.	8.00	8.51	13.52
C5H12	9.16	.	5.07	4.44	4.51
C5H10=	0.00	.	0.85	0.88	0.88
C6H14	9.01	.	5.40	4.69	4.50
C6H12= & CYCLO'S	0.00	.	1.22	1.43	1.30
C7+ IN GAS	25.95	.	26.47	28.76	27.06
LIQ HC'S	0.00	.	8.76	7.40	5.72
TOTAL	100	100	100	100	100

SURGROUPING					
C1 -C4	54.89	52.23	52.40	56.03	
C5 -420 F	44.11	43.11	43.42	40.77	
420-700 F	0.00	4.55	4.18	3.20	
700-END PT	0.00	0.11	0.01	0.00	
C5 -END PT	44.11	47.73	47.60	43.97	
ISO/NORMAL MOLE RATIO					
C4	.4058	.1696	.1406	.1390	
C5	1.7590	.3791	.2706	.2586	
C6	3.9775	.9381	.7583	.8013	
C4-	.0364	.0264	.0371	.0233	
PARAFFIN/OLEFIN M RATIO					
C2	-	8.0433	5.9935	6.1552	
C3	2.3504	.8821	.7708	.8087	
C4	1.4181	.5156	.4439	.2825	
C5		5.8073	4.3862	4.9774	
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL	OIL	OIL	
DENSITY					
N, REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG-F	NO	311	328	328	NO
16	SAM	330	353	351	
50	PLR	405	430	438	LIQ-
84		551	515	541	
90		645	541	569	UID
RANGE(16-84 %)		221	162	190	
WT % @420 F		60.0	46.7	43.5	---
WT % @700 F		95.2	98.7	99.9	---

TABLE 9B RESULT OF SYNGAS OPERATION

RUN NO.	10011-7				
CATALYST	UCC-201. (FR-UCC-101), #9673-11C 80 CC 62.0GM				
FEED	H2:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10011-7-6	10011-7-7	10011-7-8	10011-7-9	10011 7-10
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	92.4	100.1	116.4	123.7	140.2
PRESSURE, PSIG	305	303	306	302	299
TEMP. C	250	251	251	281	280
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.75	7.667	16.25	7.333	17.167
EFFLNT GAS LITER	353.3	152.0	319.2	127.7	287.5
GM AQUEOUS LAYER	15.586	7.171	15.199	8.42	19.25
GM OIL	0.874	0.596	1.264	0.74	2.00
MATERIAL BALANCE					
GM ATOM CARBON %	91.19	93.19	91.61	94.11	87.91
GM ATOM HYDROGEN %	88.71	89.78	88.59	88.68	83.83
GM ATOM OXYGEN %	96.80	98.29	96.98	96.21	91.66
RATIO CHX/(H2O+CO2)	0.7527	0.7863	0.7750	0.9390	0.8807
RATIO X IN CHX	2.4898	2.4824	2.4821	2.6020	2.6169
USAGE H2/CO PRDCT	1.8347	1.8312	1.8218	1.5090	1.5896
K EFFLNT SHIFT REACTN	0.25	0.26	0.26	0.94	0.70
CONVERSION %					
ON CO	21.58	23.23	23.37	45.53	40.58
ON H2	23.24	24.69	24.77	37.35	35.60
ON CO+H2	22.68	24.19	24.30	40.19	37.31
PRDCT SELECTIVITY, WT %					
CH4	16.31	15.93	15.88	18.67	19.06
C2 HC'S	10.23	10.17	9.89	11.28	11.08
C3H8	6.44	6.40	6.34	10.68	11.01
C3H6=	7.79	7.69	7.63	6.54	5.39
C4H10	3.97	3.85	3.93	6.43	6.43
C4H8=	8.59	8.34	8.46	6.51	6.35
C5H12	4.42	4.37	4.29	6.16	6.58
C5H10=	1.03	0.98	1.02	0.53	0.55
C6H14	4.88	4.52	4.50	5.64	5.78
C6H12= & CYCLO'S	1.62	1.48	1.52	0.88	0.84
C7+ IN GAS	28.53	27.41	27.54	20.05	18.00
LIQ HC'S	6.19	8.88	9.02	6.62	8.94
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	53.32	52.38	52.12	60.11	59.31
C5 -120 F	43.86	42.74	42.92	36.20	35.98
420-700 F	2.82	4.44	4.73	3.38	4.13
700-END PT	0.00	0.44	0.23	0.30	0.58
C5 -END PT	47.68	47.62	47.88	39.89	40.69
ISO/NORMAL MOLE RATIO					
C1	.1286	.1189	.1098	.1907	.1249
C5	.2213	.2093	.1874	.4287	.3269
C6	.6647	.6521	.6149	1.1677	.9331
C4-	.0419	.0210	.0437	.0518	.0443
PARAFFIN/OLEFIN M RATIO					
C2	7.0118	5.6982	6.3539	13.0454	13.7128
C3	.7894	.7940	.7931	1.5576	1.9498
C4	.4456	.4463	.4483	.9528	.9772
C5	4.1575	4.3533	4.0764	11.3938	11.5267
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	"	OIL	OIL	OIL
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	321	NO	329	326	313
16	339		346	346	338
50	413	LIQ--	437	438	430
84	499		564	574	589
90	520	UID	603	624	651
RANGE(16-84 %)	160		218	228	251
WT % @420 F	54.5	---	45.0	44.3	47.3
WT % @700 F	100	---	97.4	95.4	93.5

TABLE 9C RESULT OF SYNGAS OPERATION

RUN NO. 10011-7
 CATALYST UCC-201, (FR-UCC-101), #9673-11C 80 CC 62.0GM
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-7-11	0011-7-12	0011-7-13	0011-7-14	10011-7-15
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	50:50:0	50:50:0
HRS ON STREAM	147.3	163.5	171.4	187.5	195.3
PRESSURE, PSIG	303	304	309	308	304
TEMP. C	280	281	279	280	280
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	7.083	16.25	7.917	16.083	7.75
EFFLNT GAS LITER	145.1	288.3	141.7	310.2	149.4
GM AQUEOUS LAYER	9.48	18.94	9.23	20.32	10.0
GM OIL	0.83	1.32	0.49	2.16	1.86
MATERIAL BALANCE					
GM ATOM CARBON %	107.36	95.19	92.20	99.62	101.29
GM ATOM HYDROGEN %	101.75	87.38	88.53	96.29	97.73
GM ATOM OXYGEN %	111.66	98.68	96.59	103.82	104.02
RATIO CHX/(H ₂ O+CO ₂)	0.8853	0.8949	0.8640	0.8143	0.8797
RATIO X IN CHX	2.6165	2.6487	2.6410	2.3936	2.3507
USAGE H ₂ /CO PRDCT	1.6007	1.5907	1.6190	1.3913	1.4286
K EFFLNT SHIFT REACTN	0.68	0.69	0.65	0.33	0.31
CONVERSION %					
ON CO	39.61	40.25	38.72	25.31	26.02
ON H ₂	35.14	36.46	34.65	39.48	40.52
ON CO+H ₂	36.68	37.80	36.04	32.28	33.14
PRDCT SELECTIVITY, WT %					
CH ₄	19.33	20.46	20.29	12.86	11.12
C ₂ HC'S	10.70	11.34	10.99	8.74	7.37
C ₃ H ₈	11.05	11.64	11.73	5.51	5.24
C ₃ H ₆ -	5.26	6.01	5.31	8.64	9.25
C ₄ H ₁₀	6.70	7.45	7.05	3.80	4.02
C ₄ H ₈ -	6.21	6.34	6.46	9.38	6.87
C ₅ H ₁₂	6.34	6.31	6.69	4.37	4.05
C ₅ H ₁₀ -	0.55	0.52	0.61	1.13	1.16
C ₆ H ₁₄	5.75	5.62	5.79	4.85	4.71
C ₆ H ₁₂ - & CYCLO'S	0.85	0.80	0.85	1.94	1.93
C ₇ + IN GAS	19.76	17.70	19.52	29.36	28.61
LIQ HC'S	7.51	5.81	4.71	9.42	15.65
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	59.25	63.23	61.85	48.93	43.88
C5 -420 F	36.62	33.66	35.64	46.74	48.37
420-700 F	3.86	2.93	2.38	4.17	7.48
700-END PT	0.27	0.17	0.14	0.14	0.27
C5 -END PT	40.75	36.77	38.15	51.07	56.12
ISO/NORMAL MOLE RATIO					
C4	.1156	.1394	.0971	.1503	.2061
C5	.2688	.2374	.2221	.2424	.2364
C6	.9005	.8210	.7157	.9713	1.0000
C4=	.0452	.0597	.0457	.0542	.0876
PARAFFIN/OLEFIN M RATIO					
C2	14.4465	15.3861	15.4824	4.7559	4.5547
C3	2.0065	1.8494	2.1059	.6086	.5413
C4	1.0418	1.1339	1.0539	.3908	.5646
C5	11.2621	11.7181	10.6839	3.7653	3.3839
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	327	320	328	299	302
16	346	344	348	326	329
50	435	431	433	415	419
84	561	550	545	513	540
90	611	600	591	568	577
RANGE(16-84 %)	215	206	197	187	211
WT % @420 F	45.0	46.5	46.0	54.0	50.5
WT % @700 F	96.4	97.0	97.5	98.5	98.3

TABLE 9D RESULT OF SYNGAS OPERATION

RUN NO.	10011-7				
CATALYST	UCC-201. (FE-UCC-101), #9673-11C 80 CC 62.0GM				
FEED	H2:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHV				
RUN & SAMPLE NO.	10011-7-16	0011-7-17	0011-7-18	0011-7-19	10011-7-20
FEED H2:CO:AR	50:50:0	50:50:0	50:50:0	50:50:0	50:50:0
HRS ON STREAM	211.6	217.9	236.4	242.4	259.7
PRESSURE, PSIG	308	308	302	302	308
TEMP. C	281	280	281	282	281
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	16.25	6.25	18.583	6.0	17.25
EFFLNT GAS LITER	299.1	114.6	334.5	106.7	312.7
GM AQUEOUS LAYER	21.74	8.12	25.03	7.64	23.06
GM OIL	2.92	1.01	3.22	1.26	2.51
MATERIAL BALANCE					
GM ATOM CARBON %	94.70	94.26	93.44	95.89	91.37
GM ATOM HYDROGEN %	100.08	98.87	98.58	94.11	104.55
GM ATOM OXYGEN %	97.55	96.91	97.00	98.79	94.58
RATIO CHX/(H2O+CO2)	0.8830	0.8868	0.8572	0.8808	0.8772
RATIO X IN CHX	2.3513	2.3484	2.3567	2.3504	2.3655
USAGE H2/CO PRODT	1.3597	1.3777	1.3255	1.3027	1.2766
K EFFLNT SHIFT REACTN	0.42	0.40	0.45	0.44	0.60
CONVERSION %					
ON CO	31.02	29.84	31.85	31.33	35.65
ON H2	41.85	41.05	42.40	43.60	41.74
ON CO+H2	36.59	35.58	37.27	37.41	38.90
PRDT SELECTIVITY, WT %					
CH4	11.49	11.41	12.09	11.94	12.87
C2 HC'S	7.86	7.91	7.89	7.96	8.33
C3H8	4.82	5.00	4.95	5.26	5.01
C3H6=	8.22	8.79	8.62	9.00	9.45
C4H10	3.32	3.41	3.27	3.49	3.34
C4H8=	9.18	9.53	9.38	9.79	10.02
C5H12	3.71	3.72	3.57	3.72	3.58
C5H10=	1.14	1.21	1.21	1.25	1.33
C6H14	4.64	4.43	4.33	4.31	4.21
C6H12= & CYCLO'S	2.20	2.05	2.05	1.91	2.10
C7+ IN GAS	32.56	32.45	32.11	28.67	31.53
LIQ HC'S	10.84	10.09	10.52	12.70	8.23
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	44.90	46.05	46.21	47.44	49.02
C5 -420 F	50.06	49.01	48.95	46.21	47.09
420-700 F	4.88	4.41	4.43	5.35	3.39
700-END PT	0.16	0.53	0.41	1.00	0.50
C5 -END PT	55.10	53.95	53.79	42.56	50.98
150/NORMAL. MOLE RATIO					
C4	.1460	.1396	.1379	.1360	.1286
C5	.2249	.2152	.1973	.2064	.1838
C6	.8454	.8592	.8364	.9435	.8422
C4-	.0580	.0571	.0588	.0603	.0608
PARAFFIN/OLEFIN M RATIO					
C2	4.3504	4.4229	4.6339	4.2000	4.3368
C3	.5595	.5430	.5475	.5573	.5063
C4	.3497	.3449	.3367	.3441	.3220
C5	3.1550	2.9871	2.8673	2.8864	2.6272
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	292	302	294	300	297
16	315	329	314	327	318
50	413	421	412	420	415
84	538	569	546	600	575
90	576	627	601	674	648
RANGE (16-84 %)	223	240	232	273	257
WT % @420 F	53.5	49.7	54.0	50.0	52.7
WT % @700 F	98.5	94.4	96.1	92.1	93.9

TABLE 9E RESULT OF SYNGAS OPERATION

RUN NO. 10011-7
 CATALYST UCC-201, (FE-UCC-101), #9673-11C 80 CC 62.0GM
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-7-21 10011-7-22

FEED H ₂ :CO:AR	50:50:0	60:30:10
HRS ON STREAM	266.7	283.6
PRESSURE, PSIG	304	304
TEMP. C	281	313

FEED CC/MIN	400	400
HOURS FEEDING	7.0	16.917
EFFLNT GAS LITER	126.9	279.42
GM AQUEOUS LAYER	9.32	13.4
GM OIL	1.36	0.89

MATERIAL BALANCE

GM ATOM CARBON %	98.27	94.94
GM ATOM HYDROGEN %	95.38	89.96
GM ATOM OXYGEN %	101.67	96.82
RATIO CHX/(H ₂ O+CO ₂)	0.8649	0.9573
RATIO X IN CHX	2.3438	3.1287
USAGE H ₂ /CO PRD'T	1.3064	1.2032
K EFFLNT SHIFT REACTN	0.41	5.48

CONVERSION %

ON CO	30.92	72.42
ON H ₂	43.94	46.61
ON CO+H ₂	37.33	55.53

PRD'T SELECTIVITY, WT %

CH ₄	12.24	42.41
C ₂ HC'S	7.81	17.59
C ₃ H ₈	4.83	14.47
C ₃ H ₆ =	8.96	2.24
C ₄ H ₁₀	3.23	6.07
C ₄ H ₈ =	9.53	1.78
C ₅ H ₁₂	3.62	3.84
C ₅ H ₁₀ =	1.30	0.10
C ₆ H ₁₄	4.05	2.61
C ₆ H ₁₂ = & CYCLO'S	2.01	0.14
C ₇ + IN GAS	30.80	6.19
LIQ HC'S	11.62	2.55

TOTAL	100	100
-------	-----	-----

SUBGROUPING

C1 - C4	46.60	84.56
C5 - 420 F	47.16	13.51
420-700 F	5.24	1.67
700-END PT	1.00	0.26
C5 - END PT	53.40	15.44

ISO/NORMAL MOLE RATIO

C4	.1249	.2048
C5	.1880	.7897
C6	.8861	2.2782
C4-	.0617	.0689

PARAFFIN/OLEFIN M RATIO

C2	4.2710	38.9135
C3	.5150	6.1746
C4	.3276	3.2815
C5	2.7122	36.3111

LTO HC COLLECTION

PHYS. APPEARANCE	OIL	OIL
------------------	-----	-----

DENSITY

N. REFRACTIVE INDEX

SIMULATED DISTILLATION

10 WT % @ DEG F	300	372
16	327	398
50	435	501
84	607	653
90	677	702

RANGE (16-84 %)	280	255
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WT % @420 F	46.3	24.3
WT % @700 F	91.7	89.8

RUN NO. 10011-07

Figure 42

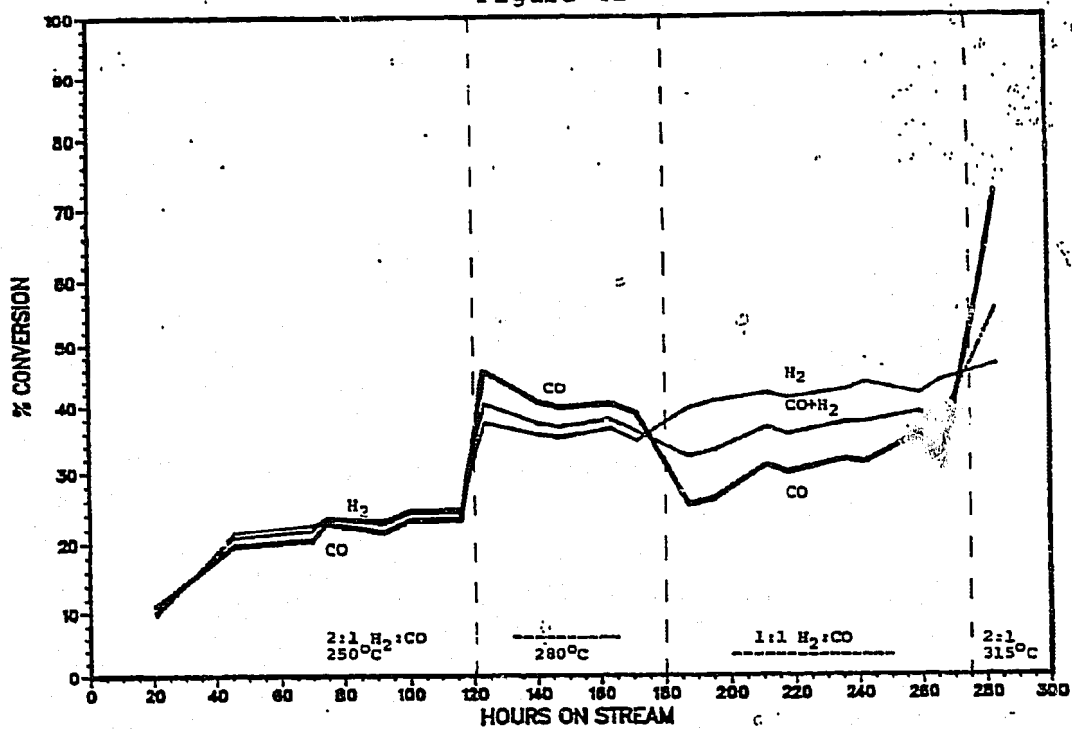


Figure 43

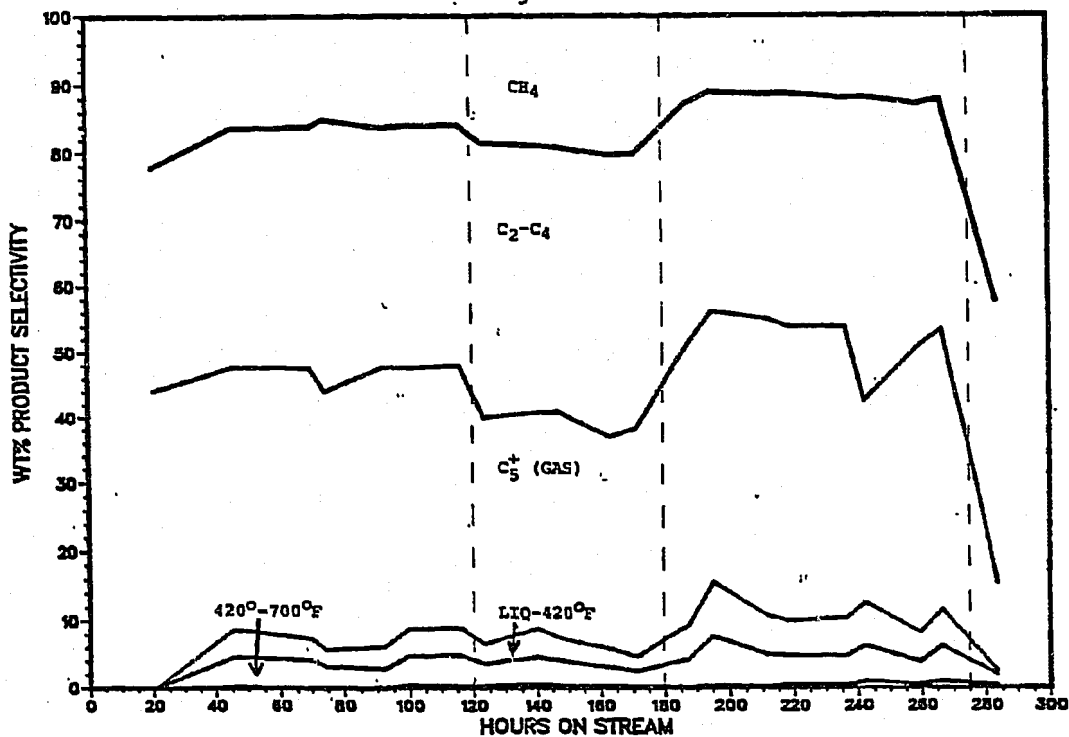
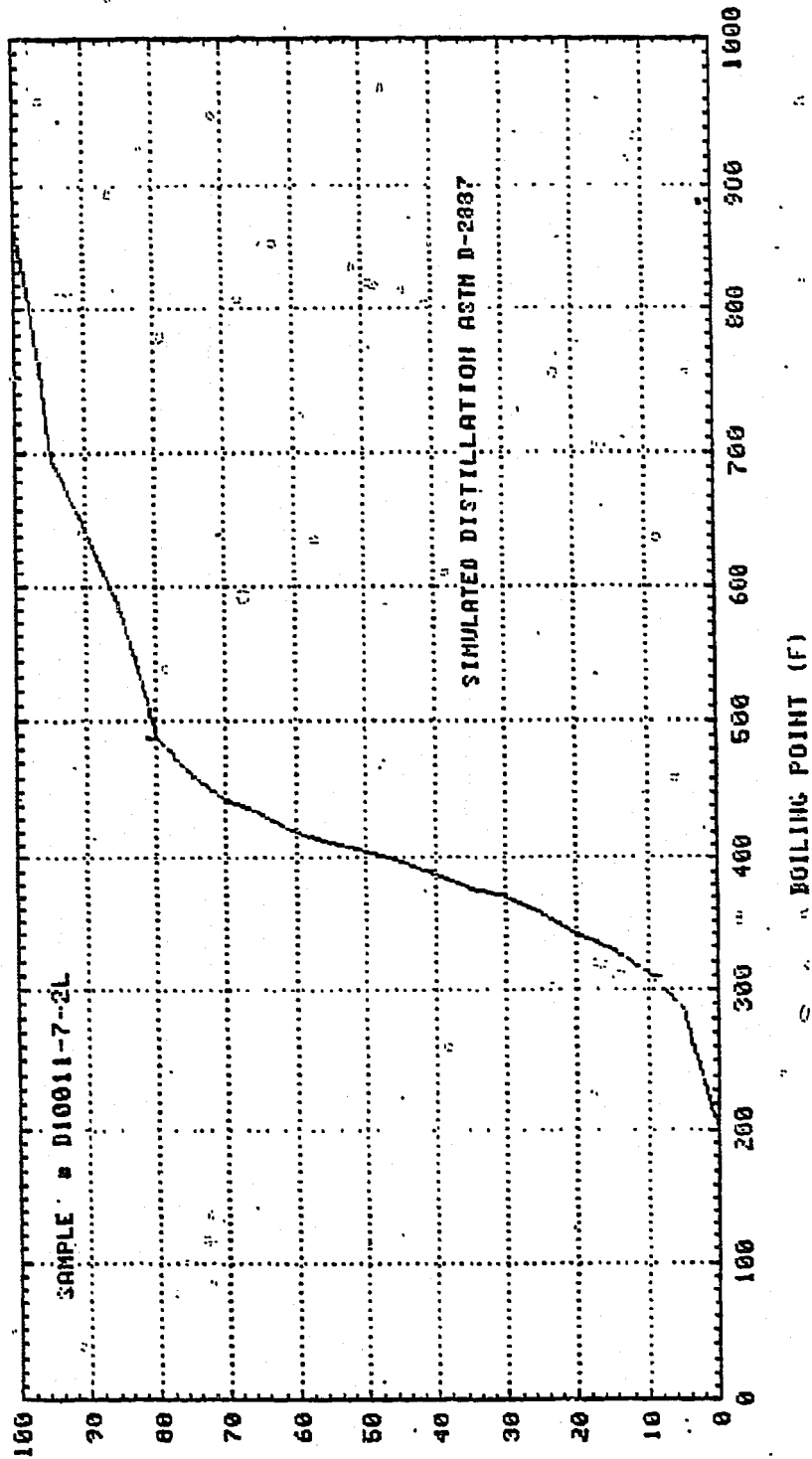


Figure 44



WT % DISTILLED

Figure 45

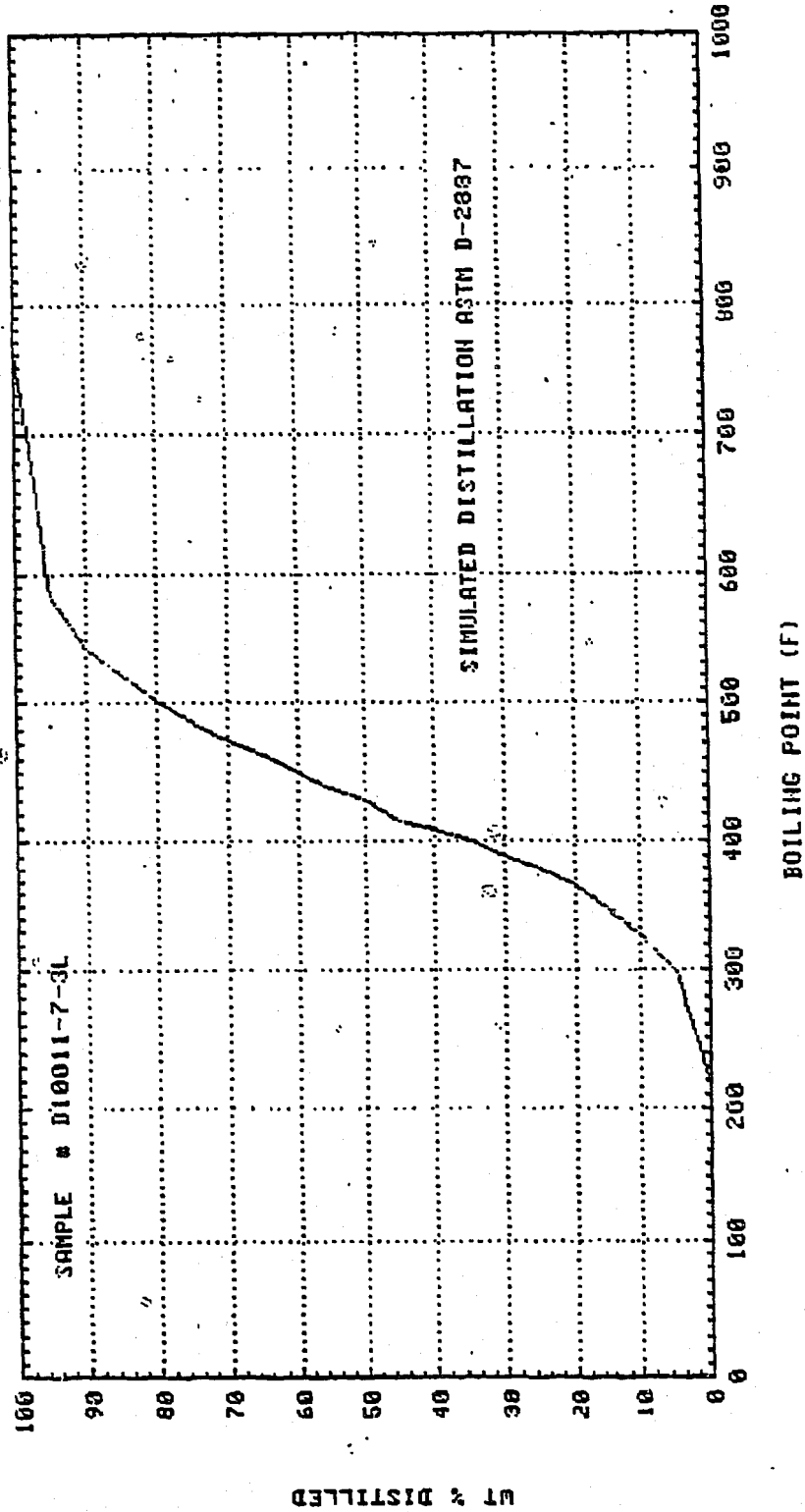
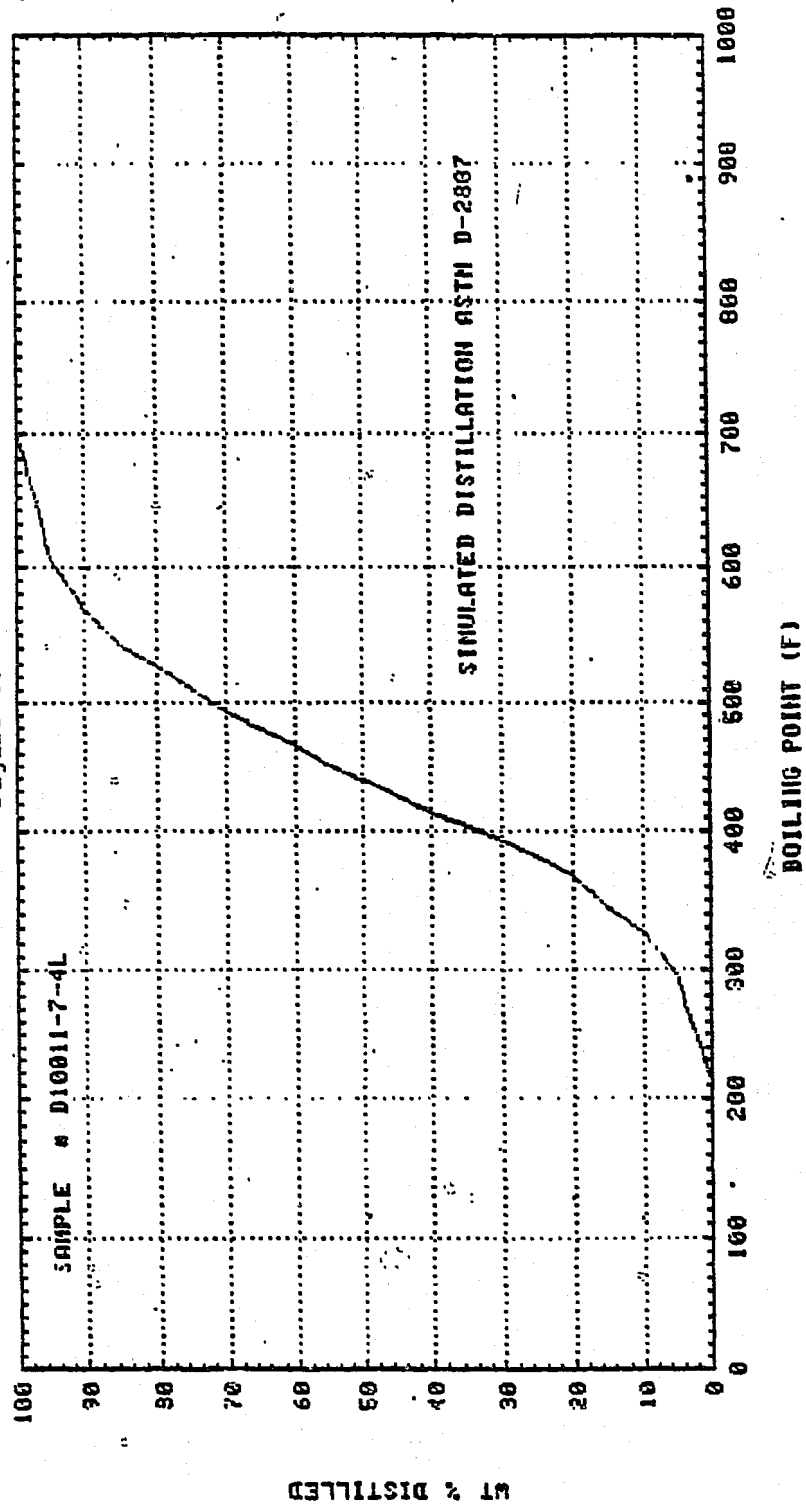
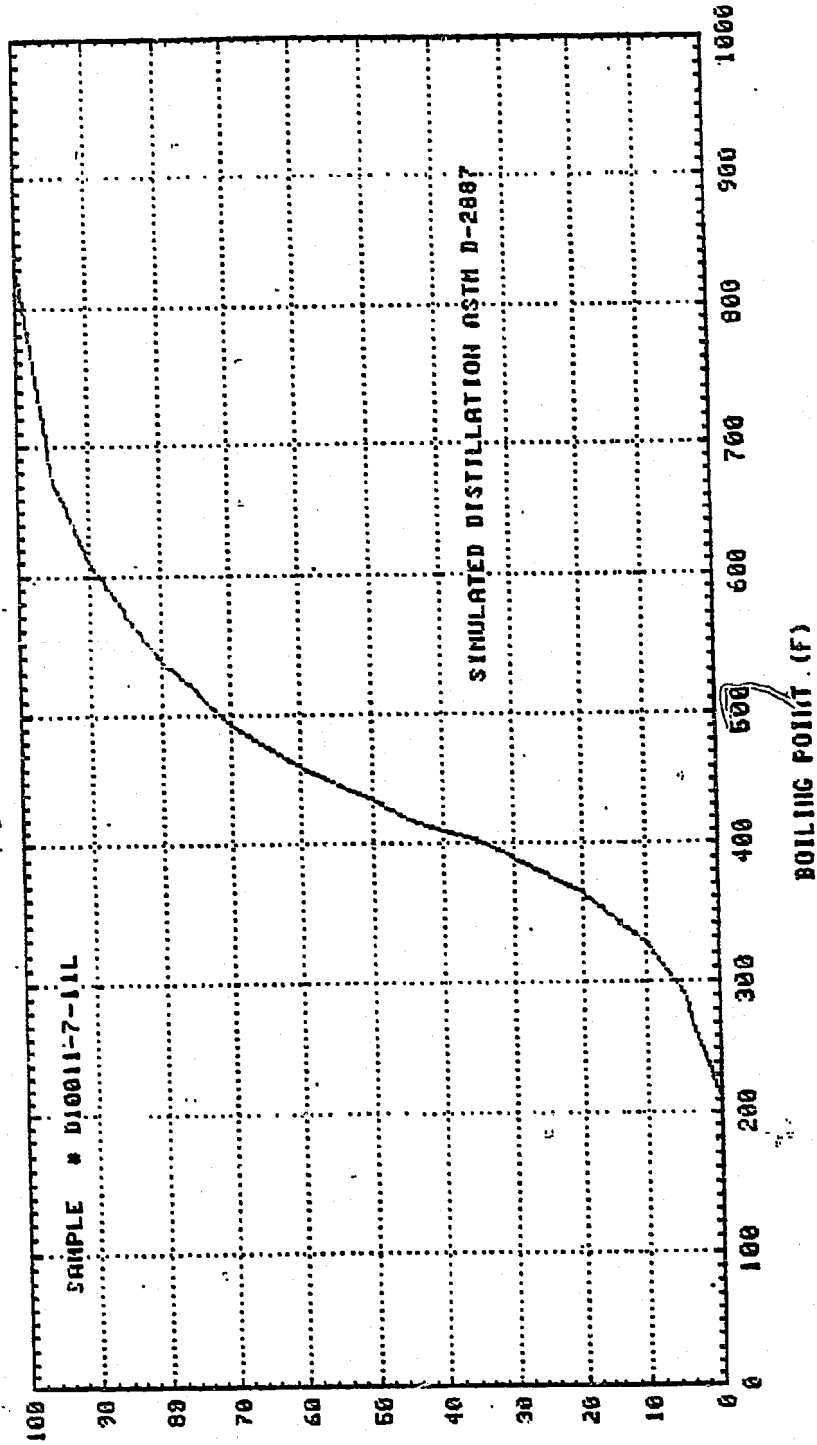


Figure 46



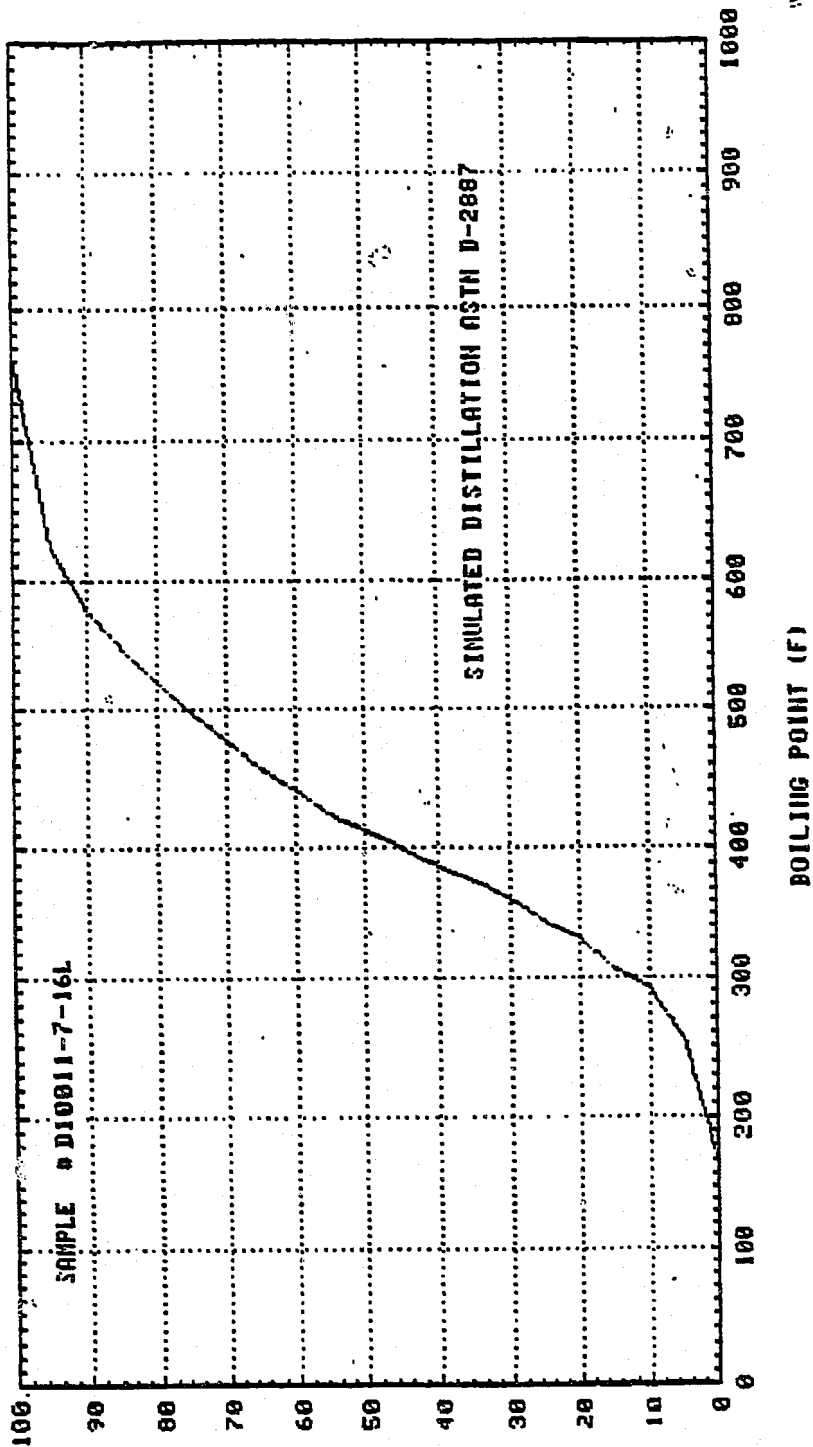
WT % DISTILLED

Figure 47



WT % DISTILLED

Figure 48



WT % DISTILLED

Figure 49

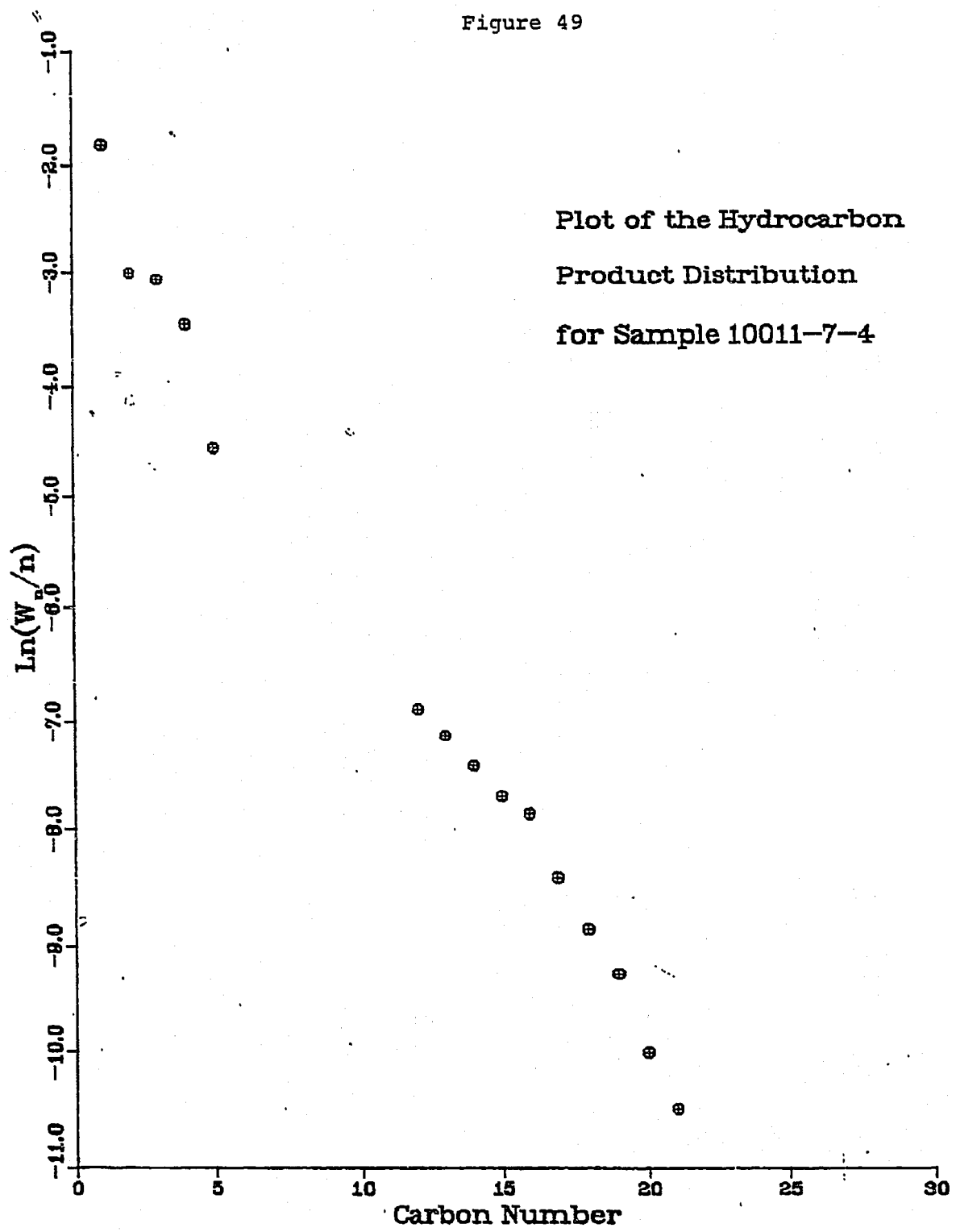


Figure 50

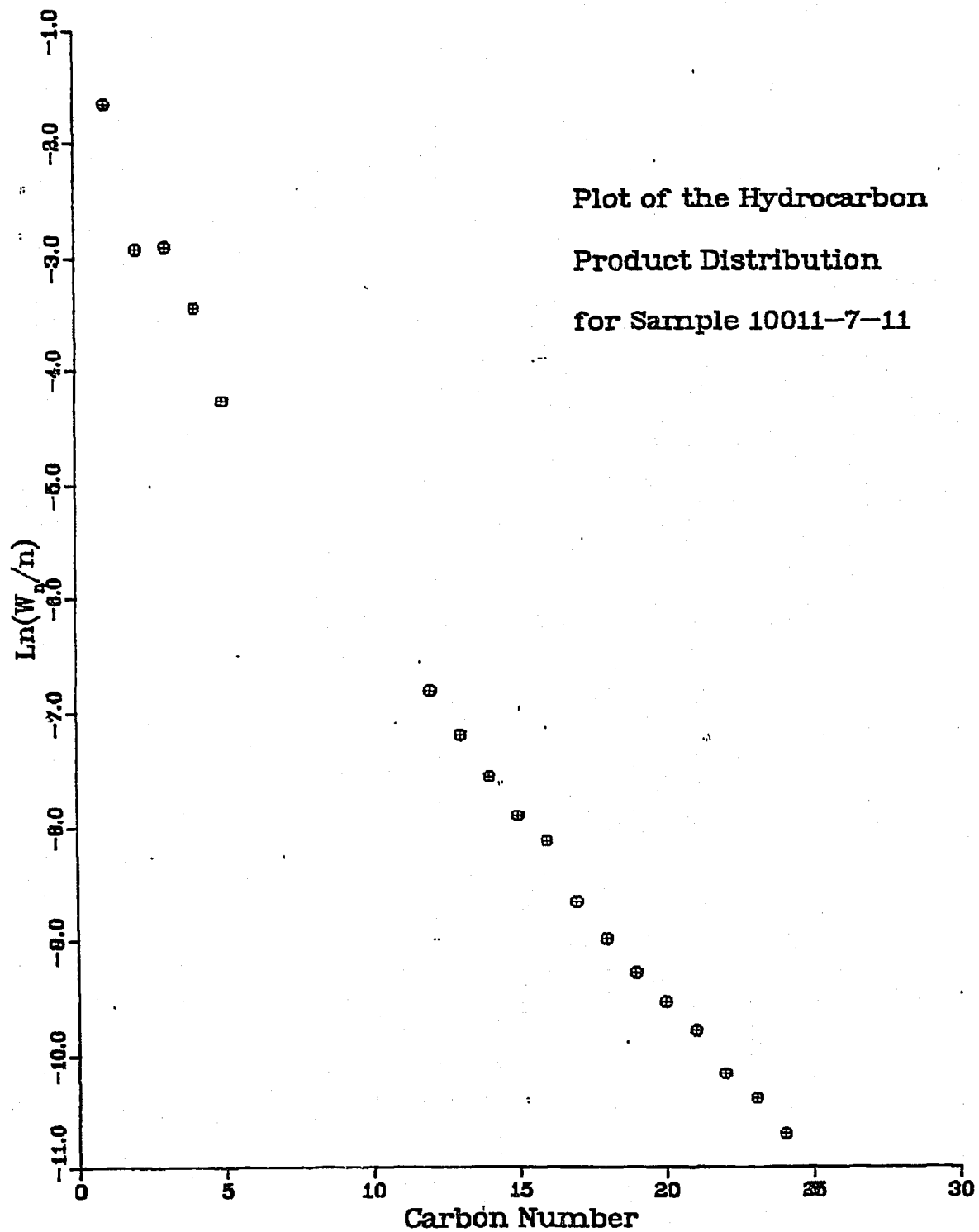
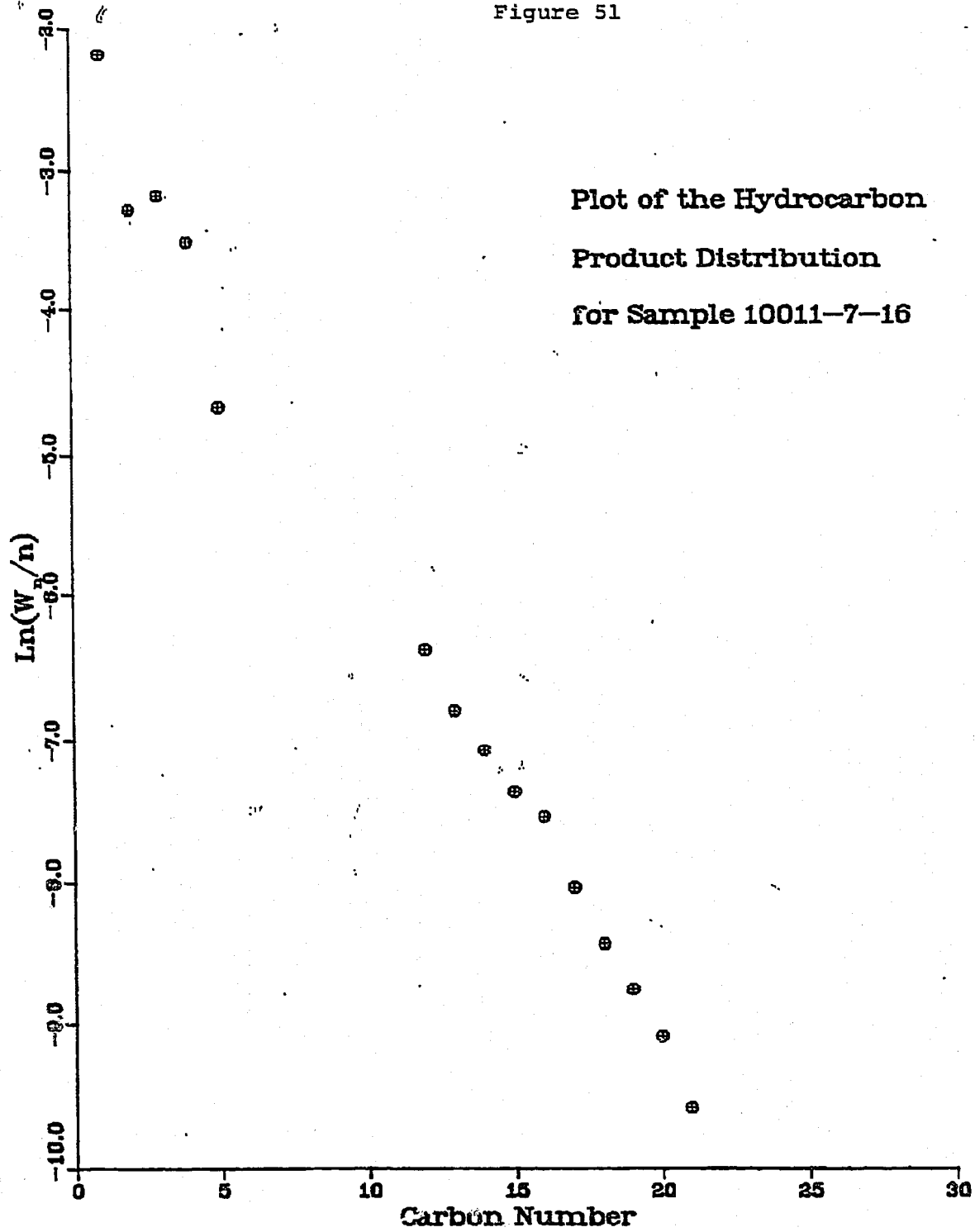


Figure 51



RUN 10011-8:Fe + UCC-101 PHYSICAL MIXTURE

This catalyst consisted of a physical mixture of potassium-promoted iron and UCC-101. Some of the same lot of reference iron catalyst as was tested in run 10011-6 was ground with a mortar and pestle. That powder was well mixed with an equal weight of UCC-101 powder and the mixture pressed into pellets. In this catalyst the iron and molecular sieve were not in as intimate contact as they were in the previous catalyst where the iron was precipitated onto the molecular sieve. It was hoped that even in a physical mixture the components might be close enough for the molecular sieve to react with reaction intermediates from the metal and transform them into desired products. It was hoped that this would eliminate the heavy waxes without destroying the selectivity to motor fuels. It was also assumed that the grinding of the metal component and the slightly different process condition would not affect the product distribution greatly.

The material balances, conversions and hydrocarbon product selectivities are presented in tables 10A to 10G. Plots of the conversion and product selectivity versus time on stream are presented in figures 52 and 53. Plots of the simulated boiling point distributions of the condensed products from samples representative of the process conditions employed are presented in figures 54 to 58. Figures 59 to 63 show the hydrocarbon product distribution of those representative samples.

This run like run 10011-6 was quite extensive. The catalyst was on-stream for 17 days. The initial conditions used were 250°C with 1:1 H₂:CO syngas feed. These were the same conditions used in run 10011-6 when the catalyst began to form wax. This time the reactor pressure was 300P instead of 100P. This higher pressure was intended to increase conversion. As was seen in run 10011-6, the increased pressure was expected to produce heavier boiling hydrocarbons. After 100 hours on stream when the catalyst had reached a steady operation without solid wax production, the feed was switched to 2:1 syngas. This change was made to slow down any possible deactivation of the catalyst while the liquid products from the first few samples were analyzed. The results of this analysis were used to help decide on changes in the process conditions to maximize the gasoline and diesel fuel yield. The

catalyst was put in a holding pattern while the analyses were performed. When the data was obtained, the feed was switched back to 1:1 syngas to reestablish the activity of the catalyst. The reaction temperature was then lowered to 220°C to increase the diesel fuel in the liquid. However, the conversion suffered so badly by lowering temperature to 220°C that the temperature was increased to 230°C. Unfortunately this increase did not improve the conversion significantly and the run was terminated after 17 days on stream.

Generally the data from this run were satisfactory. Certain samples had significant problems and the results from these samples should be weighted with concern for reproductability. There were problems with pressure control during Sample #5 and the results are only estimated. Samples 10-13 showed only marginal quality material balances. Samples 16-18 also show experimental problems. These suspect samples however do not affect the interpretation of the results by changing process conditions. As can be seen in figures 52 and 53 the performance of the catalyst was reasonably constant at each process condition. The consistency ratio for all the samples were close to one another, indicative good experimentive data.

= The conversion of syngas was high already at 250°C. The usage ratio being less than one suggests that the catalyst could efficiently use a lower H₂:CO ratio syngas such as is produced in modern coal gasifiers. The catalytic activity was very steady and it did not show the large initial drop in conversion as this same metal catalyst itself had shown in run 10011-6. The reason for this difference is unknown. When the feed was switched to 2:1 syngas, the conversion data showed that the catalyst would not use such a hydrogen rich feed efficiently. After a week on 2:1 feed, the feed was switched back to 1:1 syngas. Little deactivation had occurred in that week since the conversion and product selectivity returned to the previous levels. At 220°C the conversion of syngas dropped to under 20%. At 230°C this increased slightly to 23%.

This catalyst had high water gas shift activity. This activity paralleled that found in F-T synthesis so that the selectivity for CO to either CO₂ or hydrocarbons remained constant. With 1:1 syngas feed at 250°C, 50% of the CO converted during the sampling period became CO₂. At 220°C this percentage was still 45%. This was in spite of the fact that the shift constant had dropped by a factor of 10. The drop in WGS activity almost exactly paralleled the loss of Fischer-Tropsch activity. The total activity of the system had dropped by a factor of 3 during this period.

The extent of chain growth was not as great with this catalyst as with the reference iron catalyst under similar conditions. The cause of this may be known after a reference physical mixture of iron with α -Al₂O₃ is tested. The methane production at 250°C with 1:1 syngas feed was 15%. This methane selectivity was three times worse than that of the reference catalyst at 250°C. It was even worse than that of the unpromoted catalyst in run 10011-7 at 280°C with 1:1 syngas. Again, this was much worse than the reference and also worse than the unpromoted iron catalyst tested under the same temperature and feed conditions.

It is to be considered, however, that this comparison with the unpromoted iron catalyst is unfair since the catalysts have very different activities. The comparisons should be made at constant conversion. Often in catalysis the price which is paid for higher conversion is a loss in selectivity. When the temperature was lowered to 220°C, the conversion was cut to a level closer to that of the unpromoted iron catalyst, but the product selectivity of this catalyst was not superior. This catalyst produced less than 10% methane. Deactivation at 220°C did hurt the product distribution leading to higher production of methane in the later samples.

Analysis of the other hydrocarbons in the gas phase gave more information about the qualities of this catalyst. The changes in selectivity of these hydrocarbons generally followed that of methane but were lesser in degree. The catalyst had a greater hydrogenation ability than that of the reference. The paraffin-olefin ratio of the C₃ and C₄ hydrocarbons was much higher in

this run than in run 10011-6. The iso-normal ratio also showed differences. Moderate differences in isomerization ability rarely show up in the C_4 and C_5 hydrocarbons because these paraffins are very difficult to isomerize. C_6 is the first paraffin which is easier to isomerize. The higher iso/normal ratio of C_{10} in this run resulted from the acid activity.

Analysis of the condensed product also added new information about the properties of this catalyst. The first observation was that the condensed hydrocarbon product was a liquid and not a solid wax. Even under conditions where the reference catalyst produced significant methane and little condensed hydrocarbon product (30P, 310°C), the condensed product was still a solid wax. The fact that the condensed product was all liquid was not due to a smaller S-F α but because the condensed product was fundamentally different. The first hint came from the lighter paraffins with the high iso/normal ratio. The chromatographs from the simulated distillation showed not only the normal hydrocarbons but also isomerized products. This was the reason why the condensed products from samples 10011-6-35 and 36 were liquid. Another reason for the product being a liquid was seen in the plots of the simulated distillations. The boiling point distributions of the condensed products of this catalyst were not as wide as were seen in run 10011-6. The product distributions based on these distillations did not show the second α starting at C_{20} as was seen in run 10011-6. The condensed product seemed to have only one α .

The products did deviate somewhat from a Schultz-Flory distribution. The missing C_6 - C_{10} data would be helpful to better define this deviation. The most obvious problem with the product distribution plot was that the C_1 - C_4 data did not fit the $C_{10}+$ data. The lights appeared to have a lower α with a change possibly in the region of missing data. The condensed liquid also showed deviation from a S-F distribution. In sample #31 there was an apparent cutoff at $\approx C_{22}$ at the upper end of the diesel

range. The most important aspect of this product distribution was that there was lower production of heavy waxes than produced with the reference catalyst. This lower wax yield helped make the product liquid instead of solid.

The C₅⁺ liquid product had other significant aspects as well. At 250°C the C₅⁺ and the gasoline portion of it were obtained in high yield. At 220°C the selectivity to motor fuels was quite good. 50% of the hydrocarbon product boiled in the gasoline range and 70% boiled in the motor fuel range, displaying excellent selectivity. A catalyst which followed a S-F distribution, maximized for motor fuels, would give a maximum of 72% products in the motor fuel range, with 46% in the gasoline range.

This catalyst, while not considered the final of this type, was very encouraging for a first attempt at a physical mixture catalyst. Many of the goals of the formulation catalyst were met. The physical mixture of the metal component and the molecular sieve gave an isomerized product, a sure indication that the sieve was influencing the product. No wax formation was observed as found with the metal component alone. In addition, the catalyst showed excellent product selectivity at 220°C. Unfortunately, the conversion under this process condition was relatively poor.

TABLE 10A RESULT OF SYNGAS OPERATION

RUN NO. 10011-8
 CATALYST REF(Fe.K) UCC-101 #10042-23 BOCC 52.9GM. +17G WT GAIN AFTER RUN
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 100 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-8-1	10011-8-2	10011-8-3	10011-8-4	10011-8-5
FEED H ₂ :CO:AR	50:50:0	50:50:0	50:50:0	50:50:0	50:50:0
HRS ON STREAM	17.13	22.08	42.61	45.74	66.0
PRESSURE, PSIG	295	294	292	296	294
TEMP. C	251	252	253	252	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.1333	4.95	20.5333	3.1333	20.25
EFFLNT GAS LITER	217.1	64.8	269.0	41.4	262.84 F
GM AQUEOUS LAYER	7.91	2.32	9.56	1.06	2.58
GM OIL	10.27	3.75	16.00	2.59	8.68
MATERIAL BALANCE					
GM ATOM CARBON %	88.14	91.08	91.82	94.15	87.40 E
GM ATOM HYDROGEN %	86.42	92.92	91.61	93.15	82.32 E
GM ATOM OXYGEN %	100.55	100.09	101.75	100.68	100.79 E
RATIO CHX/(H ₂ O+CO ₂)	0.7527	0.8196	0.8033	0.8673	0.7273 E
RATIO X IN CHX	2.4831	2.4568	2.4669	2.4618	2.6167 E
USAGE H ₂ /CO PRDCT	0.6117	0.6440	0.6359	0.6462	0.5656 F
K EFFLNT SHIFT REACTN	31.54	32.52	30.26	36.99	80.60 E
CONVERSION %					
ON CO	92.24	92.28	91.86	91.88	93.44
ON H ₂	61.94	61.37	61.99	62.28	60.71
ON CO+H ₂	77.24	76.67	76.95	77.16	77.56
PRDCT SELECTIVITY, WT %					
CH ₄	15.14	14.31	14.87	14.61	20.42 E
C ₂ HC'S	11.72	10.95	10.94	10.60	13.50 E
C ₃ H ₈	8.82	8.46	8.54	8.69	10.65 F
C ₃ H ₆ =	7.81	7.58	8.78	7.20	7.68 E
C ₄ H ₁₀	4.14	4.04	3.92	4.15	4.78 E
C ₄ H ₈ =	7.16	7.00	6.57	6.85	7.13 E
C ₅ H ₁₂	3.78	3.66	3.47	3.65	4.02 E
C ₅ H ₁₀ =	0.75	0.75	0.73	0.76	0.79 E
C ₆ H ₁₄	3.69	3.53	3.27	3.39	3.36 F
C ₆ H ₁₂ = & CYCLO'S	1.17	1.21	1.15	1.20	0.98 E
C ₇ + IN GAS	15.39	14.57	13.01	13.94	11.40 E
LIQ HC'S	20.43	23.94	24.75	24.97	15.29 E
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	54.79	52.33	53.63	52.09	54.16 F
C5 -420 F	38.26	37.68	35.81	37.00	25.77 E
420-700 F	6.76	9.05	9.33	9.04	7.40 E
700-END PT	0.18	0.93	1.23	1.87	2.68 E
C5 -END PT	45.21	47.67	46.37	47.91	35.84 E
ISO/NORMAL MOLE RATIO					
C4	.1840	.1710	.1308	.1375	.1034
C5	.3327	.3054	.2254	.2168	.1657
C6	.9652	.9557	.8128	.7651	.6869
C4-	.0459	.0497	.0570	.0594	.0665
PARAFFIN/OLEFIN M RATIO					
C2	9.0149	9.1479	10.6554	10.3347	10.7644
C3	1.0766	1.0653	.9282	1.1512	1.3241
C4	.5580	.4574	.5759	.5844	.6477
C5	4.9221	4.7233	4.6153	4.6375	4.9353
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.734	0.727	0.754	0.768	-
N. REFRACTIVE INDEX	1.4251	1.4291	1.4284	1.4300	-
SIMULATED DISTILLATION					
10 WT % @ DEG F	243	254	251	254	310
16	261	276	268	282	336
50	372	391	393	400	507
84	507	568	577	611	711
90	546	627	637	672	754
RANGE(16-84 %)	246	292	309	329	375
WT % @420 F	66.0	58.3	57.3	56.3	34.1
WT % @700 F	99.1	96.1	94.9	92.6	82.5

TABLE 10B RESULT OF SYNGAS OPERATION

RUN NO. 10011-8
 CATALYST REF (FE.K)+UCC-101 #10042-23 BOCC 52.9GM.+17G WT GAIN AFTER RUN
 FEED H2:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-8-6	10011-8-7	10011-8-8	10011-8-9	10011-8-10
FEED H2:CO:AR	50:50:0	50:50:0	50:50:0	60:30:10	60:30:10
HRS ON STREAM	72.0	89.5	97.0	114.0	120.5
PRESSURE, PSIG	299	296	299	298	296
TEMP. C	251	252	250	251	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.0	17.5	7.5	17.0	6.5
EFFLNT GAS LITER	77.5	226.7	99.7	270.1	99.1
GM AQUEOUS LAYER	2.96	8.56	3.27	16.61	4.6
GM OIL	4.33	13.37	5.78	3.50	1.1
MATERIAL BALANCE					
GM ATOM CARBON %	91.57	89.15	92.13	88.93	82.92
GM ATOM HYDROGEN %	91.46	99.52	92.40	94.65	87.51
GM ATOM OXYGEN %	101.60	88.85	100.23	103.12	92.89
RATIO CHX/(H2O+CO2)	0.8034	1.0069	0.8331	0.7568	0.8044
RATIO X IN CHX	2.4589	2.4857	2.4650	2.7007	2.7108
USAGE H2/CO PRDCT	0.6376	0.7660	0.6503	0.9045	0.8827
K EFFLNT SHIFT REACTN	32.71	22.26	24.57	27.69	33.03
CONVERSION %					
ON CO	92.85	89.92	89.62	91.98	91.69
ON H2	62.76	61.59	60.96	42.48	40.86
ON CO+H2	77.82	74.98	75.27	58.30	57.20
PRDCT SELECTIVITY, WT %					
CH4	14.20	15.33	14.77	22.54	22.87
C2 HC'S	11.16	11.55	10.62	15.06	15.00
C3H8	8.69	8.90	8.59	12.09	12.39
C3H6	7.60	6.99	6.61	4.82	4.85
C4H10	4.04	4.08	4.13	5.50	5.81
C4H8	7.13	6.78	6.61	5.38	5.45
C5H12	3.65	3.63	3.65	4.58	4.81
C5H10	0.85	0.79	0.81	0.57	0.58
C6H14	3.58	3.48	3.37	3.99	4.08
C6H12 & CYCLO'S	1.31	1.22	1.16	0.90	0.85
C7+ IN GAS	15.04	14.76	15.11	14.72	14.60
LIQ HC'S	22.69	22.49	24.54	9.85	8.72
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	52.88	53.63	51.34	65.39	66.37
C5 -C20 F	36.93	36.92	37.71	29.43	28.75
420-700 F	7.51	8.07	9.52	4.52	4.04
700-END PT	2.68	1.37	1.42	0.97	0.85
C5 -END PT	47.12	46.37	48.66	34.61	33.63
ISO/NORMAL. MOLE RATIO					
C4	.1301	.1106	.1036	.0972	.0976
C5	.2102	.1782	.1651	.1585	.1531
C6	.7887	.6631	.5989	.4990	.5026
C4=	.0645	.0646	.0628	.0766	.0766
PARAFFIN/OLEFIN M RATIO					
C2	9.6246	10.6564	11.2464	17.2140	17.3085
C3	1.0907	1.2142	1.2396	2.3934	2.4368
C4	.5433	.5813	.6031	.9873	1.0283
C5	4.1956	4.4461	4.3756	7.8760	8.1260
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.758	0.758	0.747	0.767	-
N. REFRACTIVE INDEX	1.4305	1.4274	1.4293	1.4328	-
SIMULATED DISTILLATION					
10 WT % @ DEG F	256	254	257	295	313
16	285	280	290	320	333
50	402	391	403	447	446
84	634	578	590	656	650
90	734	642	647	698	698
RANGE(16-84 %)	349	298	300	336	317
WT % @420 F	55.1	58.0	55.4	44.3	44.0
WT % @700 F	88.2	93.9	94.2	90.2	90.3

TABLE 10C RESULT OF SYNGAS OPERATION

RUN NO. 10011-8
 CATALYST REF(Fe,K)+UCC-101 #10042-23 80CC 52.9GM, 117G WT GAIN AFTER RUN
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-8-11	0011-8-12	0011-8-13	0011-8-14	10011 8-15
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	137.0	145.0	161.8	169.1	186.1
PRESSURE, PSIG	292	301	295	294	297
TEMP. C	250	250	252	252	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	16.5	8.0	16.75	7.25	17.0
FEEDNT GAS LITER	255.5	123.8	259.5	112.8	264.9
GM AQUEOUS LAYER	12.15	5.80	12.49	5.45	12.09
GM OIL	3.08	1.44	2.98	0.94	2.98
MATERIAL BALANCE					
GM ATOM CARBON %	83.45	81.29	80.95	86.77	87.68
GM ATOM HYDROGEN %	89.47	88.00	87.68	90.76	91.79
GM ATOM OXYGEN %	95.38	91.94	91.19	92.22	92.71
RATIO CHX/(H ₂ O+CO ₂)	0.7719	0.7906	0.7981	0.8932	0.9014
RATIO X IN CHX	2.7384	2.7089	2.7113	2.6730	2.6819
USAGE H ₂ /CO PRD'T	0.8734	0.8874	0.8970	0.9383	0.9316
K FEEDNT SHIFT REACTN	32.43	32.81	33.43	31.59	34.39
CONVERSION %					
ON CO	91.40	91.77	92.12	92.18	92.37
ON H ₂	40.14	40.30	40.76	42.75	42.37
ON CO+H ₂	56.44	56.56	56.98	58.74	58.53
PRD'T SELECTIVITY, WT %					
CH ₄	24.07	22.69	22.85	20.70	21.14
C ₂ HC'S	15.46	14.78	14.79	13.26	13.38
C ₃ H ₈	12.38	12.59	12.58	14.03	14.01
C ₃ H ₆ =	4.27	4.41	4.11	4.72	4.50
C ₄ H ₁₀	5.68	5.86	5.92	6.63	6.47
C ₄ H ₈ =	4.92	5.12	4.87	5.69	5.42
C ₅ H ₁₂	4.67	4.87	4.82	5.59	5.43
C ₅ H ₁₀ =	0.50	0.53	0.49	0.53	0.51
C ₆ H ₁₄	4.00	4.23	4.06	4.81	4.57
C ₆ H ₁₂ = & CYCLO'S	0.78	1.11	2.14	0.84	0.84
C ₇ + IN GAS	13.53	14.36	14.11	17.21	15.69
LIQ HC'S	9.74	9.45	9.25	5.98	8.06
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 - C4	66.78	65.45	65.12	65.03	64.91
C5 - 420 F	28.06	29.31	29.84	31.65	30.70
420-700 F	3.94	4.09	3.90	2.68	3.51
700-END PT	1.22	1.14	1.15	0.64	0.88
C5 - END PT	13.22	34.55	34.88	34.97	35.09
ISO/NORMAL MOLE RATIO					
C4	.0913	.0917	.0871	.0903	.0866
C5	.1480	.1490	.1455	.1755	.1664
C6	.4872	.4975	.4721	.4689	.4461
C4-	.0781	.0773	.0788	.0751	.0773
PARAFFIN/OLEFIN M RATIO					
C2	19.3020	19.4736	20.5609	19.5583	21.8656
" C3	2.7661	2.7231	2.9212	2.8338	2.9746
C4	1.1145	1.1033	1.1739	1.1246	1.1533
C5	9.0139	8.9381	9.5094	10.2179	10.3740
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.768	-	0.734	-	0.761
N. REFRACTIVE INDEX	1.4320	-	1.4317	-	1.4307
SIMULATED DISTILLATION					
10 WT % @ DEG F	294	299	303	306	303
16	319	328	332	339	332
50	437	445	442	446	442
84	664	659	659	643	647
90	725	724	731	712	713
RANGE (16-84 %)	345	331	327	304	315
WT % @420 F	47.0	44.6	45.5	44.4	45.5
WT % @700 F	87.5	87.9	87.6	89.3	89.1

TABLE 10D RESULT OF SYNGAS OPERATION

RUN NO. 10011 8
 CATALYST REF (FE, K) UCC-101 M0042-23 BOCC 52.9GM. 17GWT GAIN AFTER RUN
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN, OR 300 CHSV

RUN NO. SAMPLE NO.	10011-8-16	0011-8-17	0011-8-18	0011-8-19	10011-8-20
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	192.1	209.6	215.1	235.0	241.1
PRESSURE, PSIG	293	295	294	303	293
TEMP. C	253	250	253	253	252
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.0	17.25	5.5	19.75	6.25
EFFLNT GAS LITER	93.6	270.0	84.3	305.1	94.4
GM AQUEOUS LAYER	4.21	12.16	3.9	14.43	4.12
GM OIL	0.92	2.67	0.87	3.48	1.50
MATERIAL BALANCE					
GM ATOM CARBON %	66.75?	59.60?	70.86?	88.78	89.87
GM ATOM HYDROGEN %	73.16	68.14	74.80	91.45	90.88
GM ATOM OXYGEN %	71.45	65.87	75.77	91.92	88.16
RATIO CHX/(H ₂ O+CO ₂)	0.8903	0.8465	0.8903	0.9382	1.0354
RATIO X IN CHX	2.6434	2.6267	2.6570	2.6693	2.6332
USAGE H ₂ /CO PRDCT	0.9835	1.0057	0.9690	0.9564	0.9821
K EFFLNT SHIFT REACTN	84.39?	116.51?	68.72?	32.16	33.63
CONVERSION %					
ON CO	97.60	98.46	97.01	92.43	92.64
ON H ₂	45.37	45.62	46.12	43.73	44.52
ON CO+H ₂	61.73	61.70	62.48	59.65	60.44
PRDCT SELECTIVITY, WT %					
CH ₄	20.00	19.65	20.24	20.40	18.78
C ₂ HC'S	12.57	12.20	12.69	12.70	11.69
C ₃ H ₈	13.00	11.80	13.79	14.32	13.14
C ₃ H ₆ -	4.27	3.75	4.31	4.75	3.87
C ₄ H ₁₀	6.25	5.91	6.57	7.12	10.90
C ₄ H ₈ =	5.26	6.92	5.22	5.48	4.95
C ₅ H ₁₂	5.20	5.44	5.33	5.84	5.38
C ₅ H ₁₀ =	0.49	0.48	0.47	0.51	0.45
C ₆ H ₁₄	4.66	5.36	4.69	4.74	4.64
C ₆ H ₁₂ = & CYCLO'S	0.85	0.98	0.80	0.81	0.71
C ₇ + IN GAS	18.93	18.13	17.50	15.50	15.31
LIQ HC'S	8.52	9.37	8.40	7.83	10.19
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	61.35	60.23	62.81	64.77	63.33
C5 -420 F	34.89	34.86	32.29	31.10	30.94
420-700 F	1.94	3.88	3.83	3.30	4.51
700-END PT	0.81	1.03	1.07	0.83	1.21
C5 -END PT	38.65	39.77	37.19	35.23	36.67
ISO/NORMAL MOLE RATIO					
C4	.0920	.0840	.0905	.1011	.8393
C5	.1717	.1596	.1727	.1645	.1618
C6	.4624	.4124	.4150	.4396	.4327
C4-	.0758	.0519	.0814	.0859	.0818
PARAFFIN/OLEFIN M RATIO					
C2	20.8550	20.3975	21.3972	23.8033	23.6443
C3	2.9027	3.0075	3.0567	2.8754	3.2379
C4	1.1485	0.8245	1.2151	1.2542	2.1271
C5	10.2538	10.9209	10.9801	11.0496	11.5847
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	-	0.763	-	0.758	-
N. REFRACTIVE INDEX	-	1.4301	-	1.4296	-
SIMULATED DISTILLATION					
10 WT % @ DEG F	307	300	311	302	304
16	340	326	339	331	338
50	446	434	452	437	448
84	628	639	662	636	660
90	694	717	735	708	721
RANGE(16-84 %)	288	313	323	305	322
WT % @420 F	44.2	47.6	41.7	47.2	43.8
WT % @700 F	90.5	89.0	87.3	89.4	88.1

TABLE 10E RESULT OF SYNGAS OPERATION

RUN NO. 10011-B
 CATALYST REF (FR,K) UCC-101 #10042-23 BOCC 52.9GM. +17GWT GAIN AFTER RUN
 FEED H2:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-B-21	0011-B-22	0011-B-23	0011-B-24	10011-B 25
FEED H2:CO:AR	60:30:10	60:30:10	50:50:00	50:50:00	50:50:00
HRS ON STREAM	258.9	264.1	283.3	288.3	305.4
PRESSURE, PSIG	293	297	295	297	298
TEMP. C	252	252	253	253	220
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	17.8333	5.1667	19.25	4.9167	17.0833
EFFLNT GAS LITER	275.1	77.5	263.5	68.3	346.4
GM AQUEOUS LAYER	12.4	3.52	7.44	1.76	5.23
GM OIL	3.06	1.11	11.91	3.51	5.82
MATERIAL BALANCE					
GM ATOM CARBON %	89.91	86.52	91.31	92.77	90.36
GM ATOM HYDROGEN %	92.55	89.08	95.72	96.82	94.35
GM ATOM OXYGEN %	92.37	89.43	96.40	96.57	96.55
RATIO CHX/(H2O+CO2)	0.9515	0.9407	0.8868	0.9153	0.6741
RATIO X IN CHX	2.6736	2.6722	2.4896	2.4746	2.2276
USAGE H2/CO PRDCT	0.9523	0.9465	0.6841	0.6889	0.7088
K EFFLNT SHIFT REACTN	33.20	33.48	20.68	21.80	2.40
CONVERSION %					
ON CO	92.26	92.31	86.28	86.42	28.41
ON H2	43.31	43.21	58.12	58.40	21.61
ON CO+H2	59.31	59.26	71.87	72.11	24.94
PRDCT SELECTIVITY, WT %					
CH4	20.52	20.73	14.94	14.91	7.58
C2 HC'S	12.68	12.86	9.36	9.26	5.91
C3H8	14.27	13.90	9.96	9.81	2.32
C3H6=	4.57	3.91	6.04	5.76	5.91
C4H10	7.38	6.71	4.98	4.88	2.26
C4H8=	5.56	5.05	6.88	6.67	5.09
C5H12	6.04	5.67	4.57	4.44	2.42
C5H10=	0.52	0.45	0.77	0.75	1.66
C6H14	4.86	4.70	4.10	4.04	2.29
C6H12= & CYCLO'S	0.78	0.77	1.21	1.12	1.12
C7+ IN GAS	15.27	15.44	17.16	15.98	28.63
LIQ HC'S	7.56	9.79	20.02	22.39	34.82
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 - C4	64.98	63.18	52.16	51.28	29.07
C5 - 420 F	31.02	31.54	38.85	37.93	50.08
420-700 F	3.20	4.47	7.61	9.27	18.18
700-END PT	0.08	0.82	1.38	1.52	2.68
C5 - END PT	35.02	36.82	47.84	48.72	70.93
ISO/NORMAL MOLE RATIO					
C4	.1100	.0817	.0882	.0851	.0808
C5	.1686	.1565	.1610	.1591	.1391
C6	.4383	.4051	.4638	.4558	.2540
C4 =	.0956	.0830	.0569	.0570	.0598
PARAFFIN/OLEFIN M RATIO					
C2	24.2893	22.0015	15.5710	15.5067	1.1183
C3	2.9794	3.3884	1.5748	1.6266	.3740
C4	1.2814	1.2836	.6988	.7067	.4276
C5	11.2556	12.2500	5.7629	5.7956	1.4137
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.766	..	0.759	0.762	0.775
N. REFRACTIVE INDEX	1.4294	-	1.4265	1.4278	1.4320
SIMULATED DISTILLATION					
10 WT % @ DEG F	300	302	259	263	330
16	327	333	296	297	344
50	435	440	406	412	462
84	643	620	592	607	632
90	707	678	653	663	678
RANGE(16-84 %)	316	287	296	310	288
WT % @420 F	47.0	46.0	55.1	51.8	40.1
WT % @700 F	89.4	91.6	93.1	13.2	92.3

TABLE 10F RESULT OF SYNGAS OPERATION

RUN NO. 10011-B
 CATALYST REF (P.F.K.) UCC-101 #10042-23 BOCC 52.9GM, +17G WT GAIN AFTER RUN
 FEED H₂:CO:ARGON OF 60/30/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-B-26	0011-B-27	0011-B-28	0011-B 29	10011-B 30
FEED H ₂ :CO:AR	50:50:00	50:50:00	50:50:00	50:50:00	50:50:00
HRS ON STREAM	312.1	329.6	353.2	360.5	377.3
PRESSURE, PSIG	292	295	295	301	298
TEMP. C	219	219	221	231	231
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.75	17.5	23.6667	7.3333	16.833
EFFLNT GAS LITER	139.6	359.9	509.6	160.8	364.6
GM AQUEOUS LAYER	1.75	5.11	5.39	1.25	3.77
GM OIL	2.81	7.11	6.32	1.50	4.67
MATERIAL BALANCE					
GM ATOM CARBON %	92.19	93.28	91.70	96.17	95.33
GM ATOM HYDROGEN %	96.48	96.45	96.05	98.75	98.56
GM ATOM OXYGEN %	97.03	96.91	93.75	98.64	97.82
RATIO CHX/(H ₂ O+CO ₂)	.7472	0.8067	0.8372	0.8408	0.8420
RATIO X IN CHX	2.1957	2.2303	2.3065	2.4103	2.3847
USAGE H ₂ /CO PRODT	0.7097	0.7718	0.9470	0.8328	0.8597
K EFFLNT SHIFT REACTN	2.75	2.37	1.36	2.29	2.01
CONVERSION %					
ON CO	30.13	29.88	19.22	24.58	24.68
ON H ₂	22.21	23.76	18.39	20.98	21.61
ON CO+H ₂	26.08	26.77	18.80	22.76	23.12
PRDT SELECTIVITY, WT %					
CH ₄	6.98	7.88	10.65	14.04	13.39
C ₂ HC'S	5.52	6.16	7.38	9.00	8.42
C ₃ H ₈	2.21	2.77	3.83	5.83	5.44
C ₃ H ₆	5.55	5.52	5.24	6.59	6.25
C ₄ H ₁₀	2.11	2.26	2.61	3.54	3.22
C ₄ H ₈	4.90	5.11	5.16	6.92	6.33
C ₅ H ₁₂	2.40	2.52	2.60	3.45	3.06
C ₅ H ₁₀	1.59	1.31	1.32	1.35	1.21
C ₆ H ₁₄	2.61	2.63	2.63	3.67	3.08
C ₆ H ₁₂ & CYCLO'S	1.15	1.23	1.12	1.26	1.17
C ₇ + IN GAS	26.82	27.46	24.45	24.09	21.32
LIQ HC'S	38.18	35.15	33.01	20.25	27.11
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 -C4	27.26	29.70	34.89	45.93	43.05
C5 -420 F	49.61	49.03	43.50	40.32	38.27
420-700 F	20.62	18.88	13.72	11.74	15.18
700 END PT	2.52	2.39	2.90	2.00	3.50
C5 -END PT	72.74	70.30	65.12	54.07	56.95
ISO/NORMAL MOLE RATIO					
C4	.0890	.0783	.0890	.0948	.0903
C5	.1485	.1422	.1137	.1453	.1264
C6	.4539	.3323	.2818	.4194	.4047
C4-	.0567	.0563	.0571	.0597	.0600
PARAFFIN/OLEFIN M RATIO					
C2	1.1452	2.3918	4.6955	6.2600	4.8275
C3	.3803	.4787	.6971	.8449	.8299
C4	.4160	.4272	.4888	.4943	.4917
C5	1.4678	1.8682	1.9138	2.4840	2.4581
LIQ HC COLLECTION					
PHYS. APPEARANCE	OIL	OIL	OIL	OIL	OIL
DENSITY	0.780	0.770	0.775	-	0.737
N. REFRACTIVE INDEX	1.4317	1.4315	1.4333	-	1.4345
SIMULATED DISTILLATION					
10 WT % @ DEG F	335	329	341	341	341
16	347	343	372	379	377
50	461	464	483	497	509
84	621	628	651	659	680
90	665	672	692	699	721
RANGE(16-84 %)	274	285	379	280	303
WT % @420 F	39.4	39.5	34.5	32.1	31.1
WT % @700 F	93.4	93.2	91.2	90.1	87.1

TABLE LOG RESULT OF SYNGAS OPERATION

RUN NO. 10011-8
 CATALYST REF(PF,K)-UCC-101 #10042-23 BOCC 52.9GM, +17G WT GAIN AFTER RUN
 FEED H₂:CO:ARGON/CF 50/50/10 & 50/50/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-8-31 0011-8-32 10011-8-33

	50:50:00	50:50:00	50:50:00
FEED H ₂ :CO:AR	50:50:00	50:50:00	50:50:00
HRS ON STREAM	384.0	402.3	408.5
PRESSURE, PSIG	294	304	301
TEMP. C	231	231	231

FEED CC/MIN	400	400	400
HOURS FEEDING	6.6667	18.3333	6.25
EFFLNT GAS LITER	144.8	389.0	133.45
GM AQUEOUS LAYER	1.37	3.88	1.08
GM OIL	1.47	4.99	1.48

MATERIAL BALANCE			
GM ATOM CARBON %	94.25	93.34	93.64
GM ATOM HYDROGEN %	98.26	96.34	96.55
GM ATOM OXYGEN %	97.30	95.96	96.04
RATIO CHX/(H ₂ O+CO ₂)	0.8027	0.8308	0.8424
RATIO X IN CHX	2.4155	2.3864	2.4085
USAGE H ₂ /CO PRDCT	0.8420	0.8466	0.8358
K EFFLNT SHIFT REACTN	2.09	2.08	2.28

CONVERSION %			
ON CO	23.96	24.74	24.76
ON H ₂	20.66	21.45	21.11
ON CO+H ₂	22.28	23.07	22.90

PRDCT SELECTIVITY, WT %			
CH ₄	14.37	13.44	14.04
C ₂ HC'S	9.12	8.27	9.13
C ₃ H ₈	5.74	5.38	5.61
C ₃ H ₆	5.28	5.98	6.19
C ₄ H ₁₀	3.45	3.28	3.35
C ₄ H ₈	6.63	5.96	6.27
C ₅ H ₁₂	3.36	3.15	3.19
C ₅ H ₁₀	1.34	1.20	1.16
C ₆ H ₁₄	3.11	3.03	3.36
C ₆ H ₁₂ & CYCLO'S	1.17	1.09	1.08
C ₇ + IN GAS	22.47	21.83	22.76
LIQ HC'S	22.96	27.37	23.85

TOTAL	100	100	100
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SUBGROUPING			
C1 -C4	45.59	42.32	44.59
C5 -420 F	38.57	39.42	39.46
420-700 F	12.58	14.84	13.05
700 END PT	3.26	3.42	2.91
C5 -END PT	54.41	57.68	55.41
ISO/NORMAL MOLE RATIO			
C4	.0807	.0814	.0801
C5	.1369	.1470	.1094
C6	.3806	.3800	.3694
C4=	.0593	.0574	.0575
PARAFFIN/OLEFIN M RATIO			
C2	7.2745	7.1521	7.5550
C3	.8726	.8590	.8640
C4	.5027	.5304	.5165
C5	2.4408	2.5495	2.6650
I.10 HC COLLECTION			
PHYS. APPEARANCE	OIL	OIL	OTT.
DENSITY	-	0.756	-
N, REFRACTIVE INDEX	-	1.4340	-
SIMULATED DISTILLATION			
10 WT % @ DEG F	342	340	340
16	379	370	371
50	508	491	495
84	691	678	677
90	729	718	716
RANGE(16-84 %)	312	308	306
WT % @420 F	31.0	33.3	33.1
WT % @700 F	85.8	87.5	87.8

RUN NO. 10011-08

Figure 52

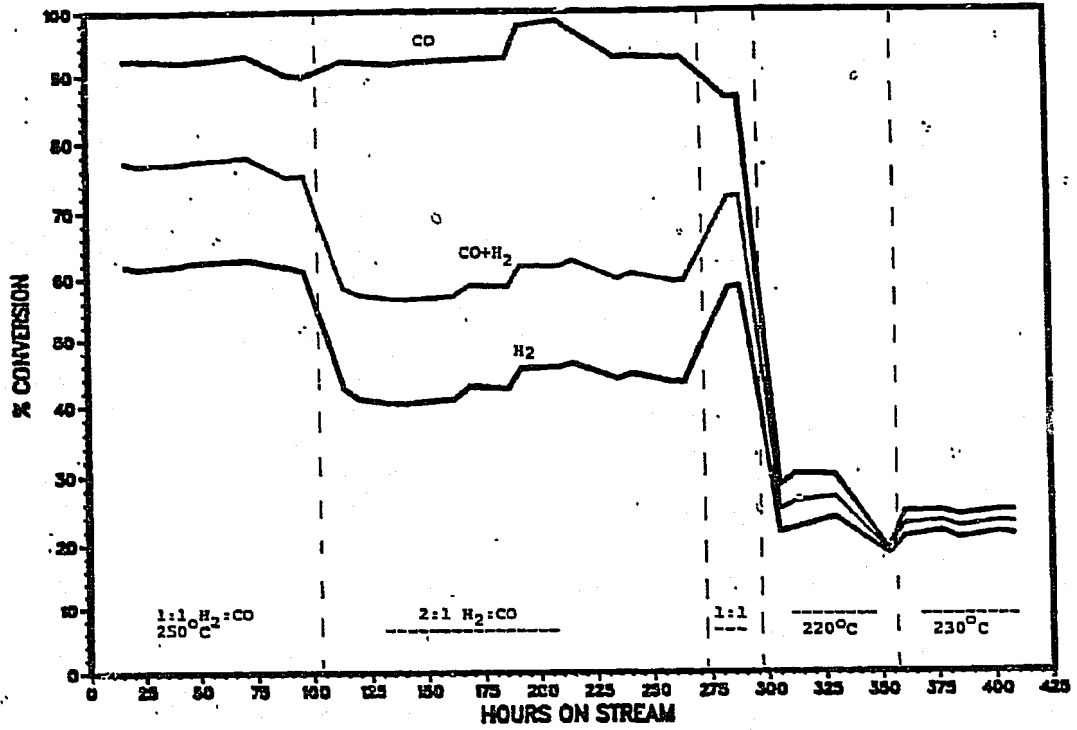


Figure 53

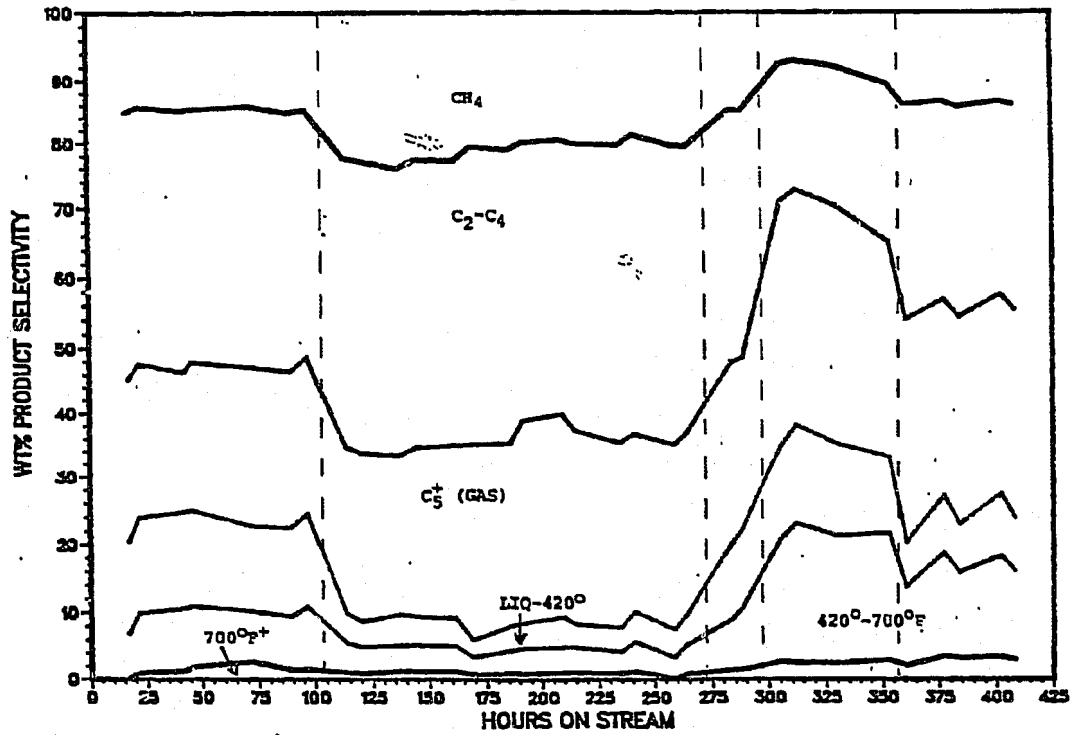
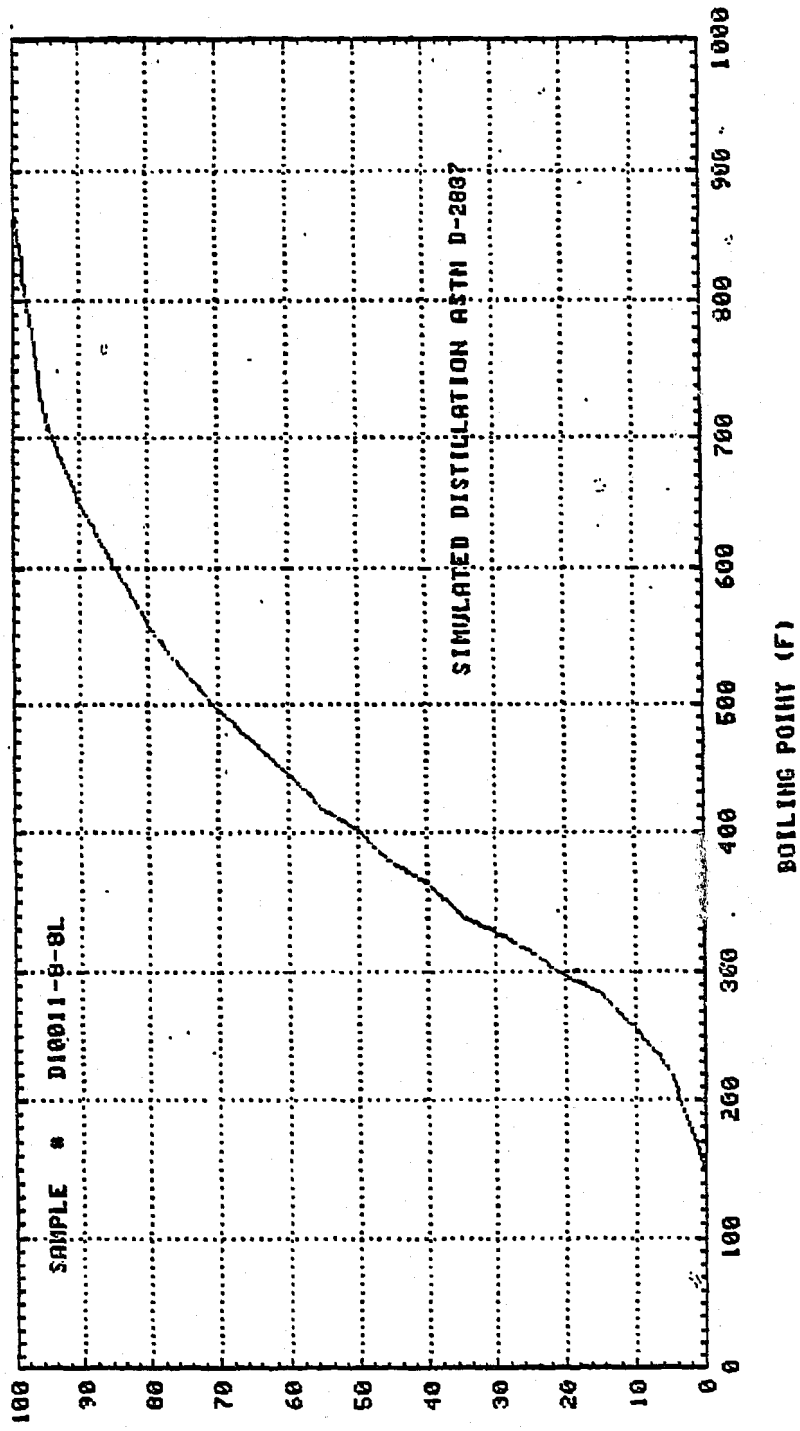


Figure 54



WT % DISTILLED

Figure 55

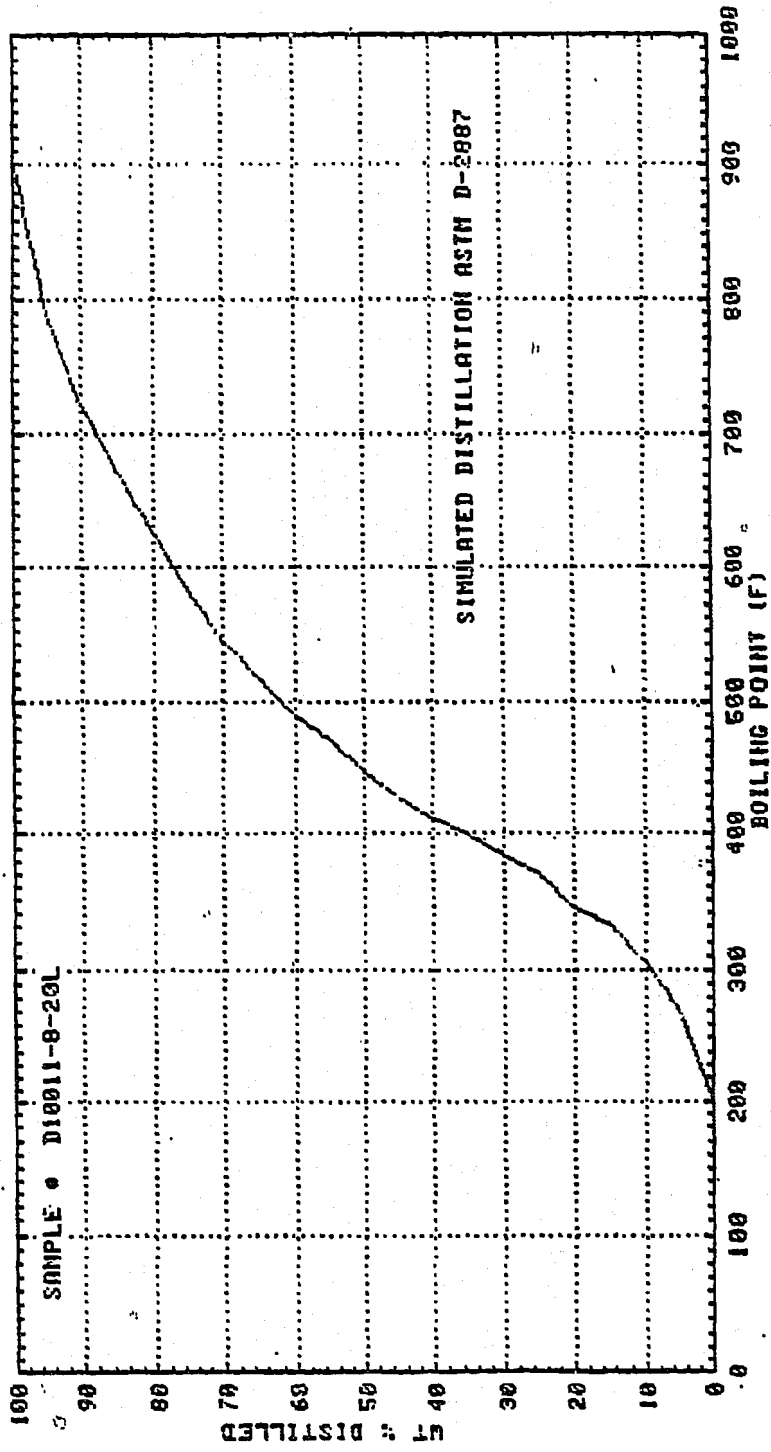


Figure 56

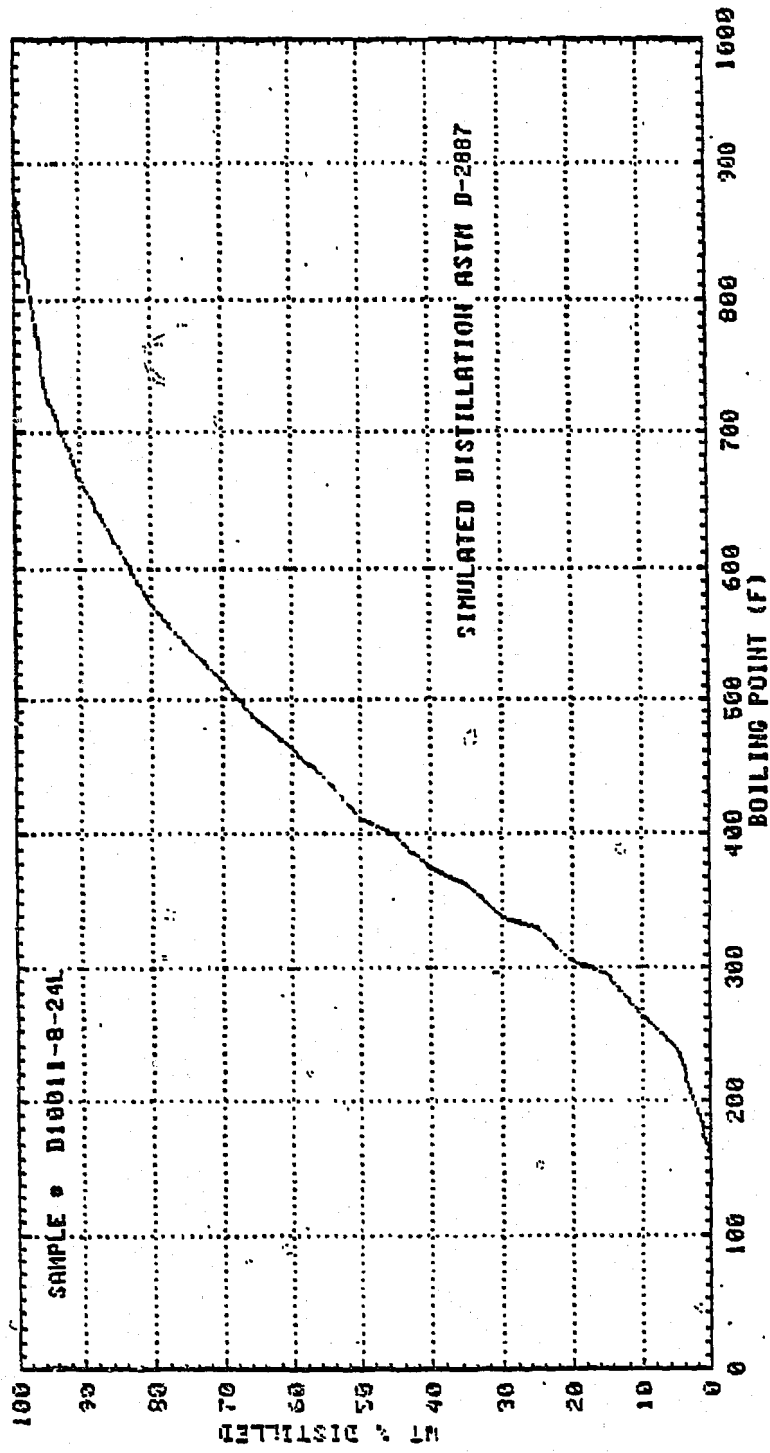


Figure 57

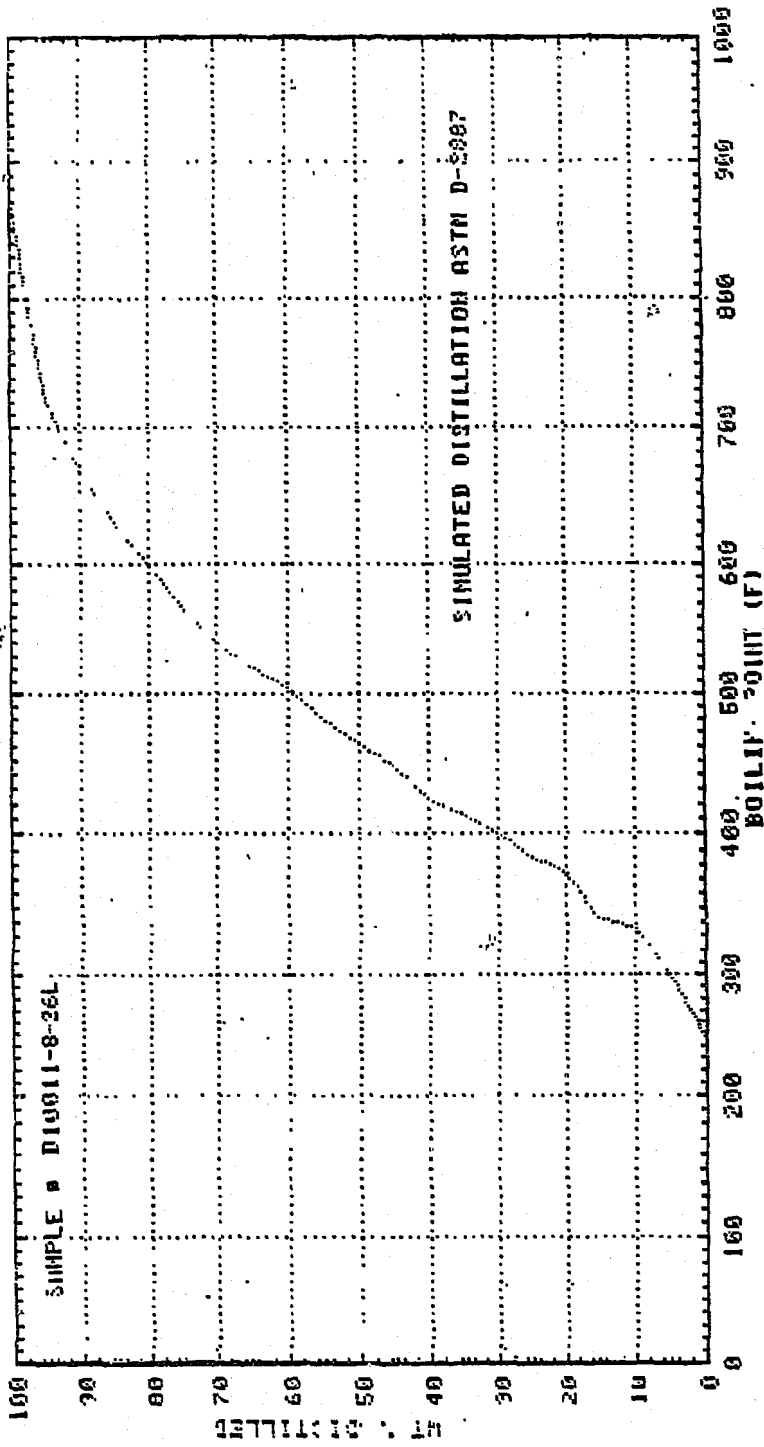


Figure 58

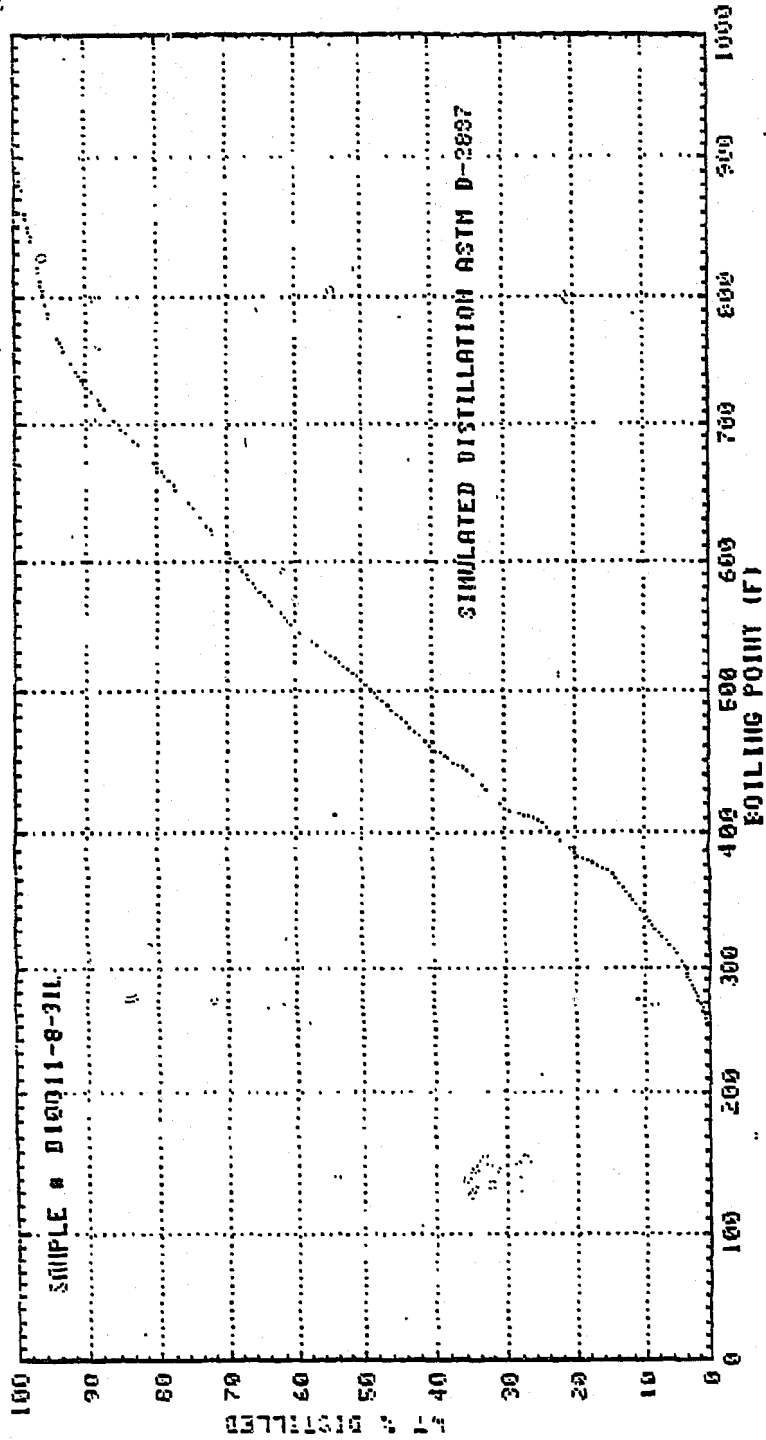


Figure 59

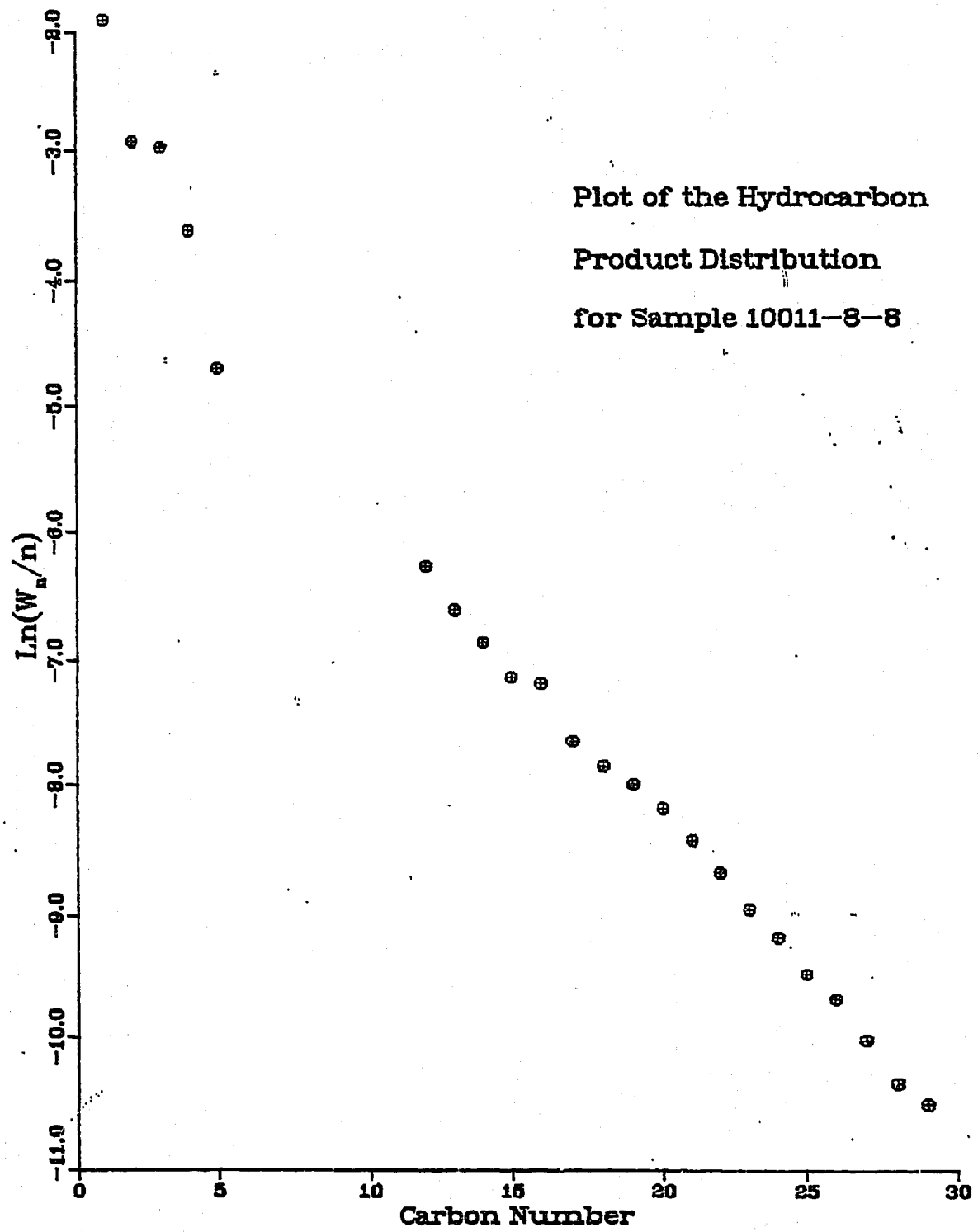


Figure 60

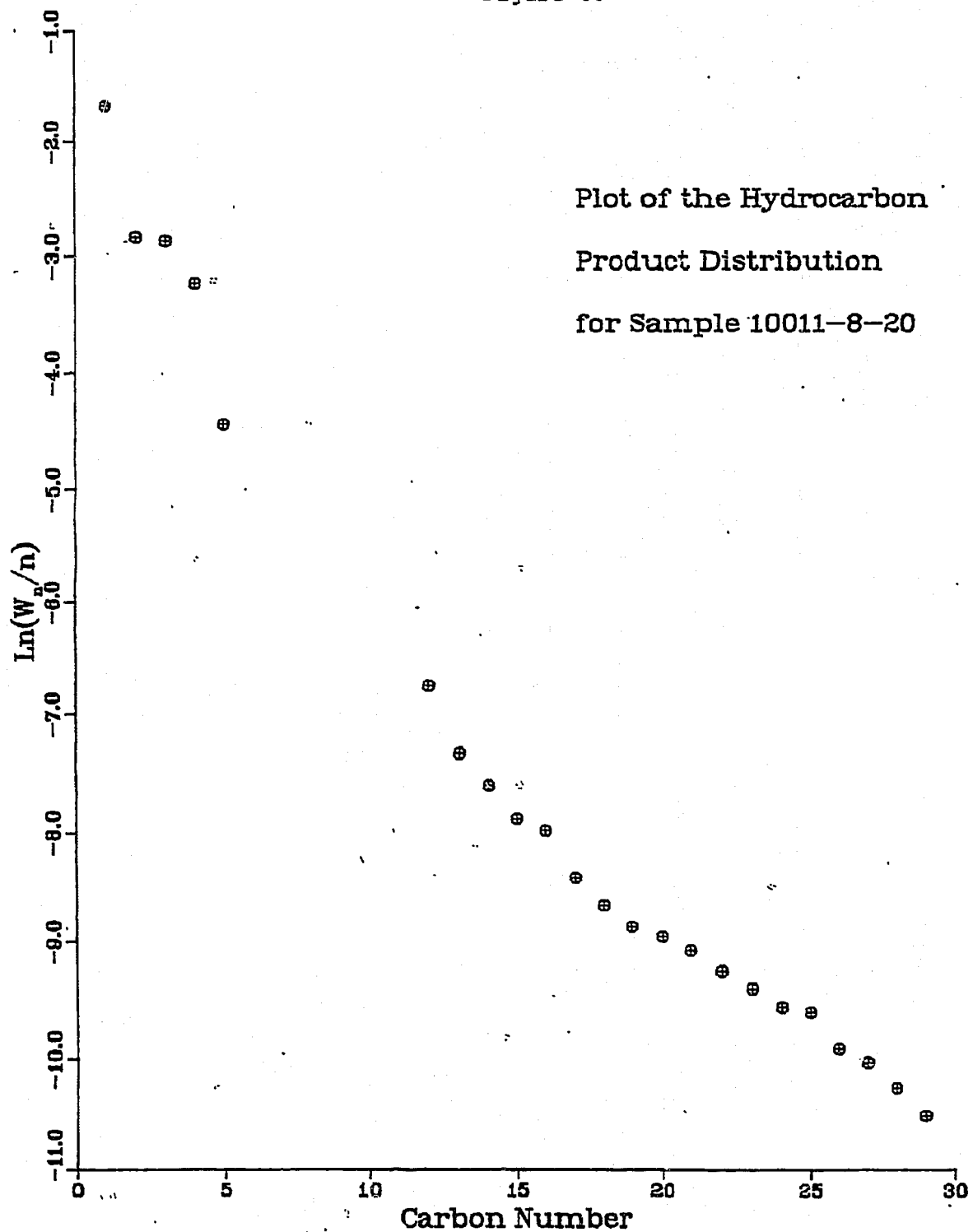


Figure 61

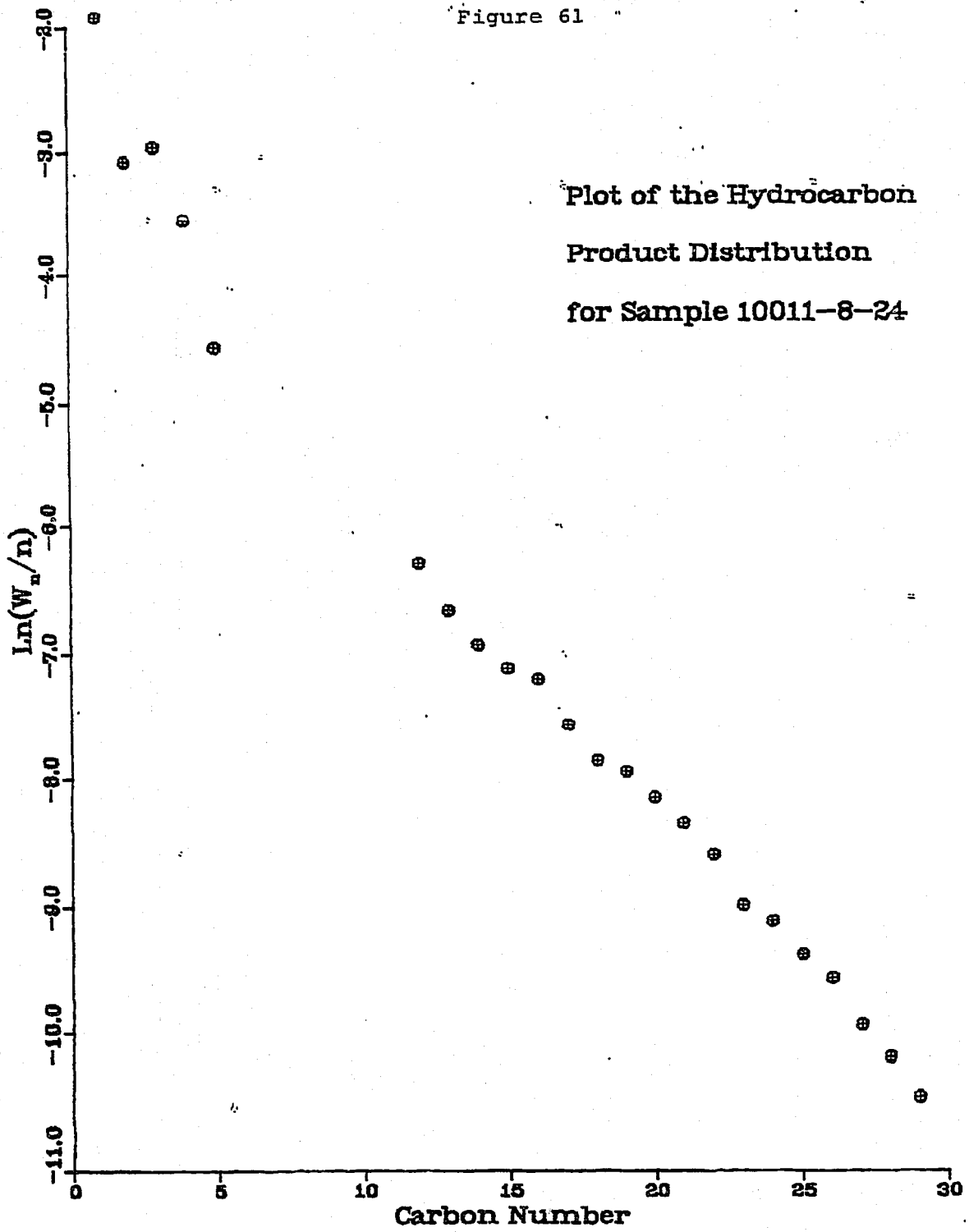


Figure 62

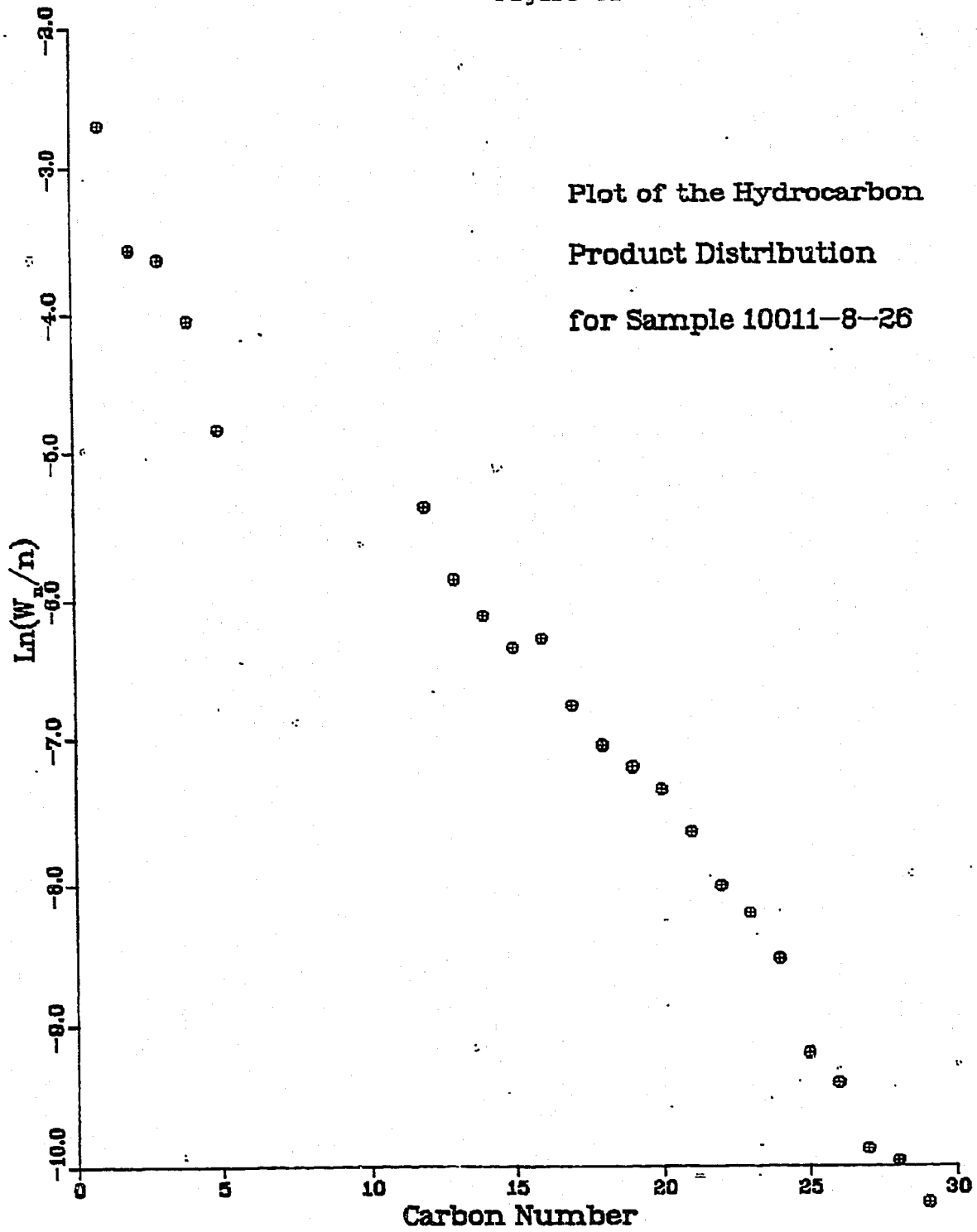
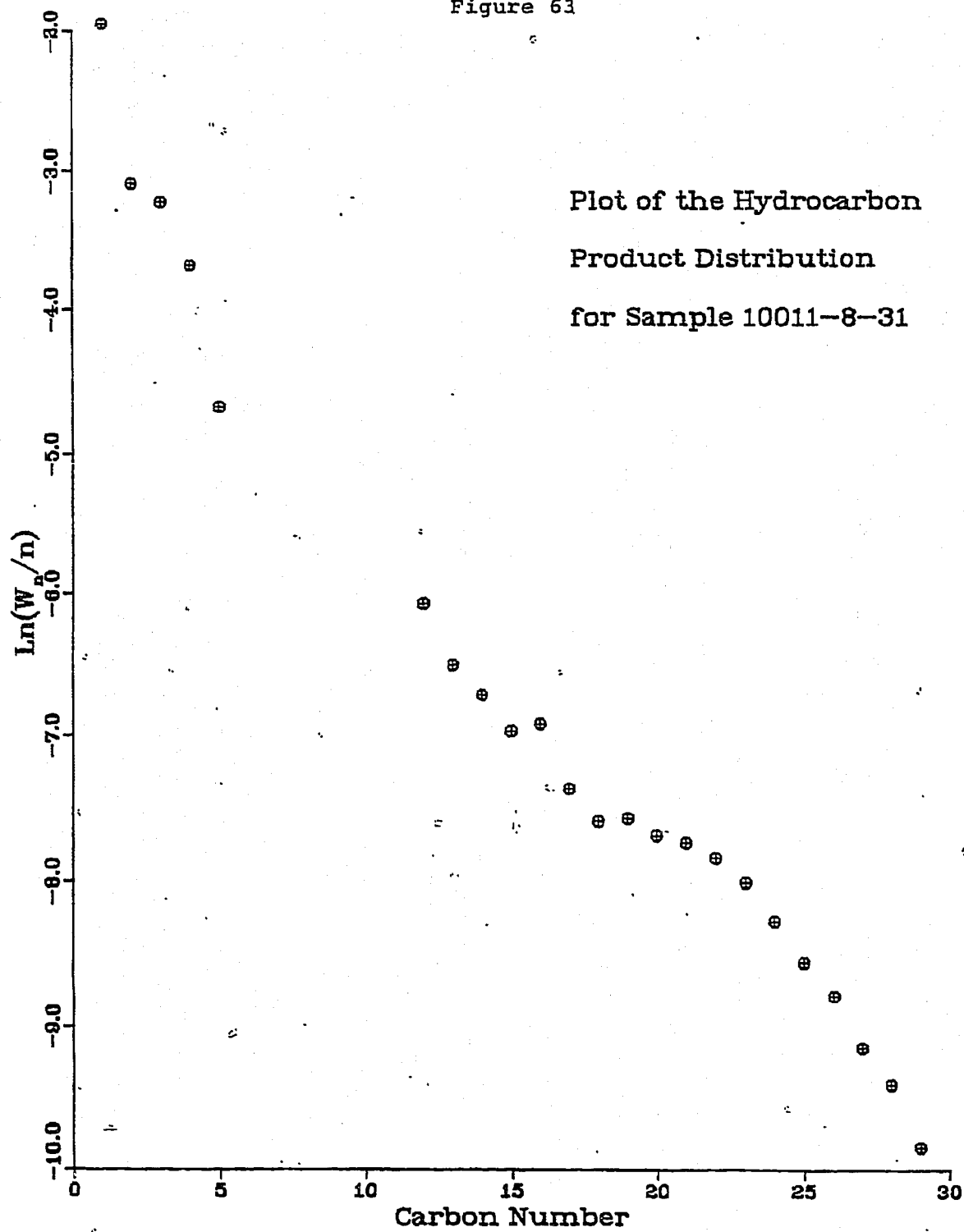


Figure 63



RUN 10011-9:Fe + UCC-101 PHYSICAL MIXTURE

This catalyst, similar to that used in the previous run 10011-8, consisted of a physical mixture of potassium-promoted iron and UCC-101. The difference was a source of the iron. Potassium-promoted, precipitated iron powder was ground slightly, mixed with an equal weight of UCC-101, pressed into pellets, and air calcined at 250°C for two hours. The evaluation of this catalyst was nowhere near as extensive as the previous catalyst. Here, only one process condition was examined. This condition was the initial condition in the previous run, 300P at 250°C with 1:1 syngas feed. The test was envisioned as a strict comparison of this catalyst's initial performance to that of the previous catalyst. These process conditions have become the standard test to evaluate iron-containing F-T catalysts.

The material balances, conversions and the hydrocarbon product selectivities of the seven samples are given in tables 11A and 11B. The conversion and selectivity data are also plotted as a function of time on stream in figures 64 and 65. The simulated distillation results of samples 3 and 5 are shown in figures 66 and 67. Plots of the product distribution of these two samples are shown in figures 68 and 69. Some of the data from this run suffer from experimental problems. The first three samples had poor material balances. Since the material balances of C, H and O are equally bad, it is conceivable that the flow rate of the feed could be lower than calculated. If the flow were lowered 17% all the material balances would be acceptable, 100±10%. This change would not affect the conversion of the product selectivity. Another explanation of the poor material balances could be a low measurement in the effluent gas flow, possibly caused by a leak before the test meter. Since the C:H:O ratio of the gaseous and condensed products are fairly equal, this error would cause changes in the conversion and product selectivity. If sample #2 were corrected for such an error, the conversion would only drop from 84% to 83%. The methane selectivity would increase to 11% and the condensed hydrocarbon selectivity decrease

to 29%. While these changes are not large, they do bring the sample more into line with samples #4 and #5. The numbers from samples #2 and #3 are probably generally correct but differences with the numbers from other samples should not be taken quantitatively.

At the beginning, the conversion was very high, but it decreased rapidly over the first two days of operation. A similar phenomenon was observed in run 10011-6. In the present run, the deactivation was even more severe; the syngas conversion leveled off at 30%. The H₂:CO ratio showed the catalyst was using the 1:1 syngas feed efficiently. The usage ratio did not change significantly over the course of the test. The constant usage ratio and fairly constant product distribution suggested that the water gas shift activity changed together with the F-T synthesis activity. The observation was also supported by calculation of the selectivity of CO to conversion to CO₂. In sample #5 this quantity was 52% and in sample #7, 48%. This selectivity was constant in spite of the fact that the total CO conversion had dropped by a factor of 2.5 and the shift constant by a factor of 5.

The product selectivity of this catalyst was not outstanding, considering the catalyst's low activity. The methane yield was 11-12% except for the two suspect samples. This selectivity was superior to that of the previous catalyst under the same process conditions. Analysis of the other gaseous hydrocarbons showed a high iso/normal ratio, as in the previous run, but the product was more olefinic than that of the last two tests. The selectivity to C₅⁺ products was particularly good only for sample #3. The 47% selectivity to gasoline and 65% selectivity to total motor fuels was close to that of a "theoretical" SF type maximum gasoline catalyst. The selectivities for the other samples were reasonable but not outstanding.

The plots of the simulated distillation of the condensed products of this run were unlike those of the other molecular sieve containing catalysts. The boiling point distribution was very broad. The catalyst did not seem to be exerting much shape selective control. The product distribution for sample #3

had minor deviations from a S-F distribution. Sample #5 had a much greater deviation from a straight line. The distribution was almost S shaped. The distribution did show some signs of a carbon number cut off.

This catalyst showed a strong initial deactivation to a steady but not highly active state. Only one of the samples showed high selectivity to gasoline and motor fuels. The other samples were marginal, the product distribution was somewhat broad but did show some signs of a carbon number cutoff.

TABLE 11A RESULT OF SYNGAS OPERATION

RUN NO.	10011-9				
CATALYST	UCC(FE,K)+UCC-101, #10042-55 80 CC 51.84 GM (68.40 G AFTER THE RUN, +16.56 GM)				
FEED	H2:CO:ARGON OF 51/49/0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10011-9-1	10011-9-2	10011-9-3	10011-9-4	10011-9-5
FRED H2:CO:AR	51/49/0	50/50/0	51/49/0	51/49/0	51/49/0
HRS ON STREAM	2.0	24.0	42.9	50.7	68.83
PRESSURE, PSIG	294	290	295	298	293
TEMP. C	253	251	250	251	250
FRED CC/MIN	400	400	400	400	400
HOURS FREDING	2.0	24.0	18.917	7.75	25.917
EFFLNT GAS LITER	21.91	296.65	287.53	153.85	517.02
GM AQUEOUS LAYER	1.35	16.20	11.51	2.832	9.47
GM OIL	1.70	20.39	12.26	2.930	9.8
f					
MATERIAL BALANCE					
GM ATOM CARBON %	75.58	79.19	79.71	92.79	92.85
GM ATOM HYDROGEN %	80.39	82.95	81.13	95.65	95.49
GM ATOM OXYGEN %	85.19	91.36	82.58	96.96	97.78
RATIO CHX/(H2O+CO2)	0.7843	0.7221	0.8754	0.8046	0.7716
RATIO X IN CHX	2.3435	2.2696	2.2351	2.3268	2.3435
USAGE H2/CO PRDCT	0.6600	0.6147	0.8714	0.7901	0.7742
K EFFLNT SHIFT REACTN	28.58	12.10	1.96	2.50	2.54
CONVERSION %					
ON CO	93.42	84.13	43.34	34.19	33.93
ON H2	58.53	53.88	36.69	27.38	27.00
ON CO+H2	74.95	68.65	39.89	30.70	30.38
PRDT SELECTIVITY, WT %					
CH4	11.17	8.65	8.00	11.13	11.72
C2 HC'S	9.67	8.28	6.70	8.53	8.78
C3H8	3.63	3.63	2.96	4.37	4.58
C3H6=	7.86	9.26	6.12	7.62	7.50
C4H10	4.27	2.44	1.88	2.63	2.75
C4H8=	5.84	7.86	5.60	7.14	6.81
C5H12	5.79	2.51	1.87	2.62	2.80
C5H10=	0.41	0.87	0.86	1.18	1.23
C6H14	5.88	3.06	1.94	2.97	3.04
C6H12= & CYCLO'S	1.57	3.44	2.60	3.10	2.96
C7+ IN GAS	11.35	14.90	18.32	19.75	18.05
LIQ HC'S	32.54	35.09	43.15	28.96	29.78
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 - C4	42.45	40.13	31.27	41.42	42.15
C5 - 420 F	42.28	42.37	46.77	42.45	38.49
420-700 F	13.37	14.42	17.90	12.53	14.18
700-END PT	2.90	3.12	4.10	3.50	5.18
C5 - END PT	57.55	59.87	68.73	58.58	57.85
ISO/NORMAL MOLE RATIO					
C4	0.7167	0.2344	0.1818	0.1675	0.1433
C5	1.7655	0.4435	0.3312	0.2857	0.2686
C6	2.6041	1.3083	0.6647	0.8581	0.8600
C4-	0.0260	0.0545	0.0620	0.0629	0.0601
PARAFFIN/OLEFIN M RATIO					
C2	1.3879	2.8107	3.4029	3.7736	4.0682
C3	0.4410	0.3742	0.4613	0.5472	0.5833
C4	0.7064	0.2993	0.3239	0.3556	0.3900
C5	13.5817	2.8007	2.1167	2.1679	2.2086
LIQ HC COLLECTION					
PHYS. APPEARANCE		CIL	OFF.		OIL
DENSITY		0.753	0.757		0.753
N, REFRACTIVE INDEX		1.4337	1.4359		1.4390
SIMULATED DISTILLATION					
10 WT % @ DEG F	NO	261	294	NO	317
16		296	319		336
50	LIQ-	420	424	LIQ-	507
84		633	649		708
90	UID	690	696	UID	746
RANGE(16-84 %)		337	330		372
WT % @420 F		---	50.0	---	35.0
WT % @700 F		---	91.1	---	82.6

TABLE 11B RESULT OF SYNGAS OPERATION

RUN NO. 10011-9
 CATALYST UCC(FE,K)+UCC-101, #10042-55 80 CC 51.84 GM
 (68.40 G AFTER THE RUN, +16.56GM)
 FEED H₂:CO:ARGON OF 51/49/0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO. 10011-9-6 10011-9-7

FEED H ₂ :CO:AR	51/49/0	50/50/0
HRS ON STREAM	75.3	95.3
PRESSURE, PSIG	296	299
TEMP. C	250	250

FEED CC/MIN	400	400
HOURS FEEDING	6.5	26.417
EFFLNT GAS LITER	130.4	526.65
GM AQUEOUS LAYER	2.29	9.32
GM OIL	2.61	10.59

MATERIAL BALANCE

GM ATOM CARBON %	93.77	93.26
GM ATOM HYDROGEN %	96.26	96.83
GM ATOM OXYGEN %	98.58	98.28
RATIO CHX/(H ₂ O+CO ₂)	0.7813	0.7772
RATIO X IN CHX	2.3432	2.3613
USAGE H ₂ /CO PRODT	0.7670	0.7548
K EFFLNT SHFT REACTN	2.69	2.83

CONVERSION %

ON CO	34.65	35.88
ON H ₂	27.25	28.04
ON CO+H ₂	30.86	31.89

PRDT SELECTIVITY, WT %

CH ₄	11.80	12.02
C ₂ HC'S	8.61	8.86
C ₃ H ₈	4.63	4.73
C ₃ H ₆	7.24	7.15
C ₄ H ₁₀	2.75	2.81
C ₄ H ₈	6.95	7.00
C ₅ H ₁₂	2.66	2.76
C ₅ H ₁₀	1.24	1.23
C ₆ H ₁₄	3.02	2.97
C ₆ H ₁₂ & CYCLO'S	2.06	2.97
C ₇ + IN GAS	17.53	17.78
LIO HC'S	30.71	29.74
TOTAL	100	100

SURGROUPING

C1 -C4	41.98	42.56
C5 -420 F	38.30	39.09
420-700 F	14.34	13.06
700 END FT	5.77	5.29
C5 -END FT	58.02	57.44

ISO/NORMAL MOLE RATIO

C4	0.1344	0.1309
C5	0.2432	0.2394
C6	0.7781	0.7417
C4 -	0.0613	0.0634

PARAFFIN/OLEFIN M RATIO

C2	4.0245	4.3454
C3	0.5102	0.6314
C4	0.3823	0.3874
C5	2.0909	2.1837

LIO HC COLLECTION

PHYS. APPEARANCE

OIL CLOUDY

DENSITY

N. REFRACTIVE INDEX

SIMULATED DISTILLATION

10 WT % @ DEG F	NO	312
16		327
50	LIQ-	494
84		713
90	UID	754

RANGE(16-84 %)	---	386
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WT % @420 F	---	38.3
WT % @700 F	---	82.2

RUN NO. 10011-09

Figure 64

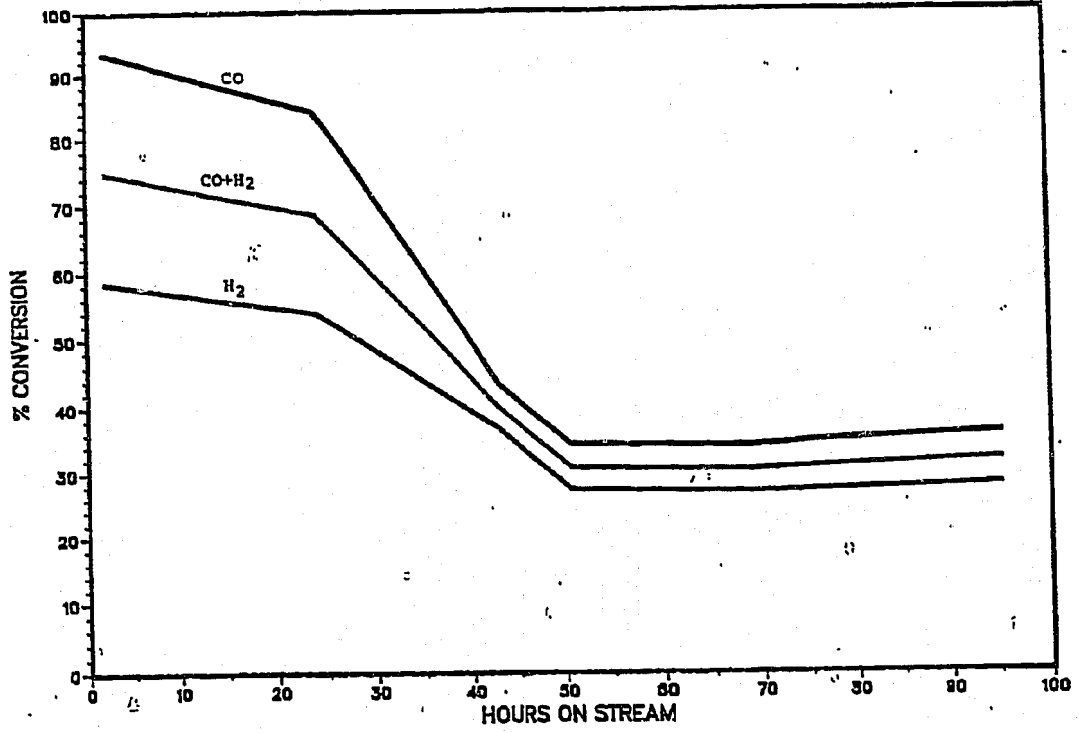


Figure 65

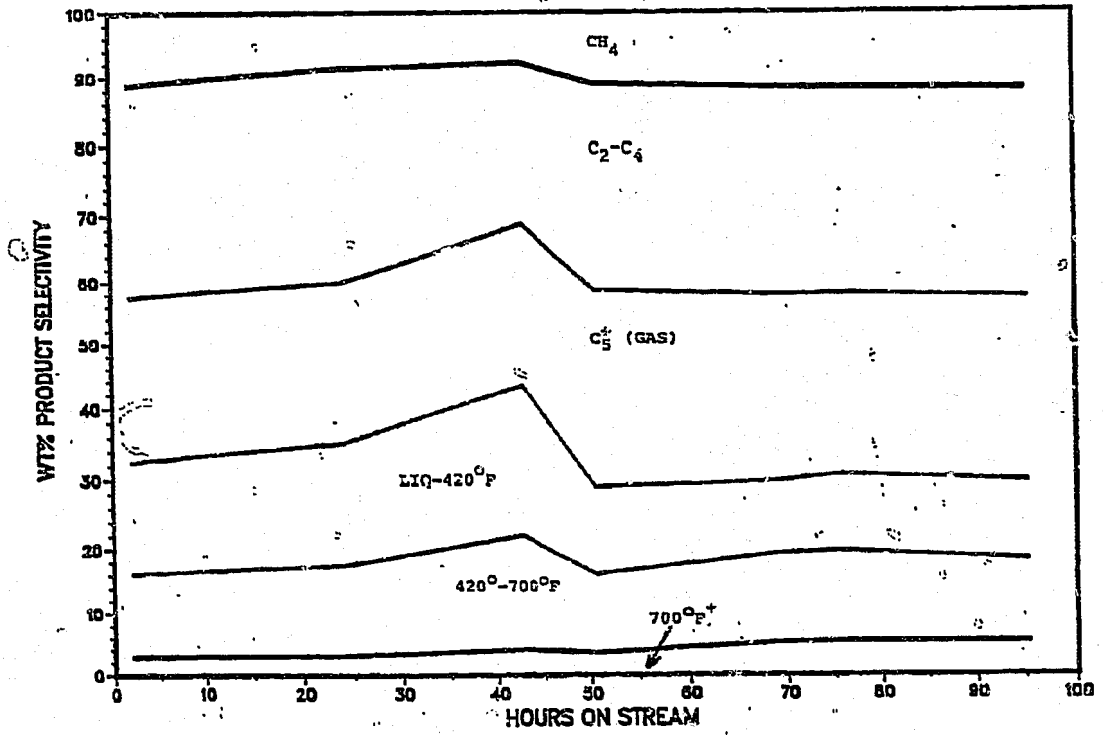
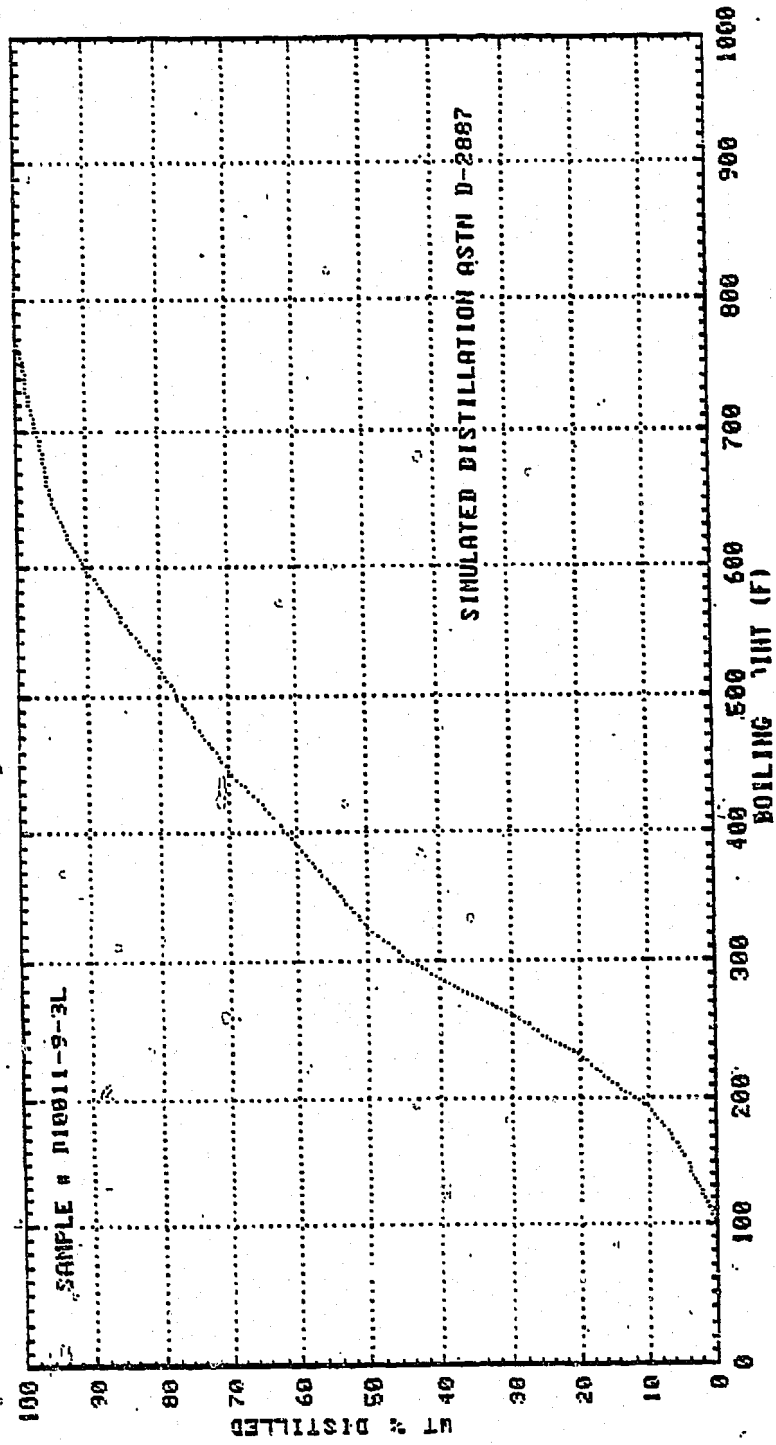
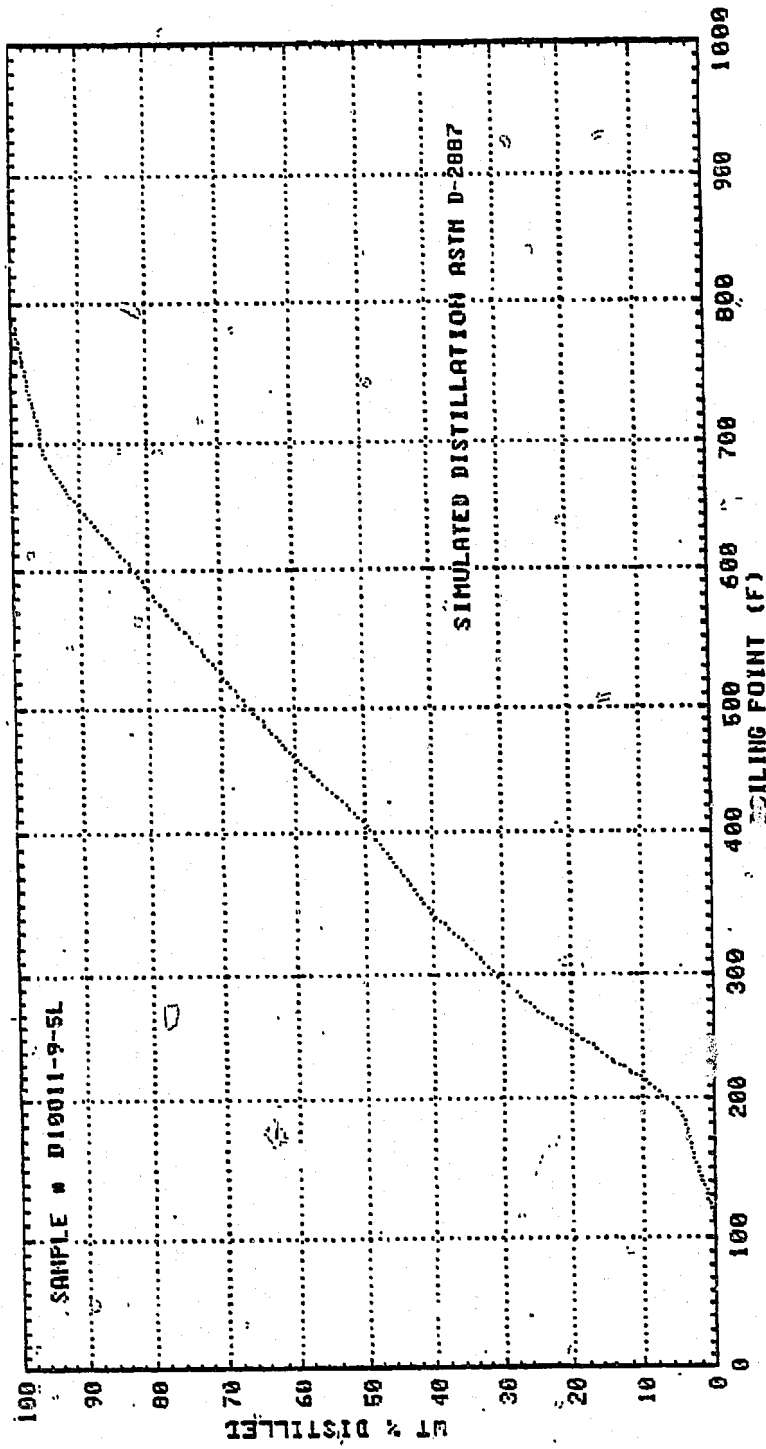


Figure 66



Figures 67



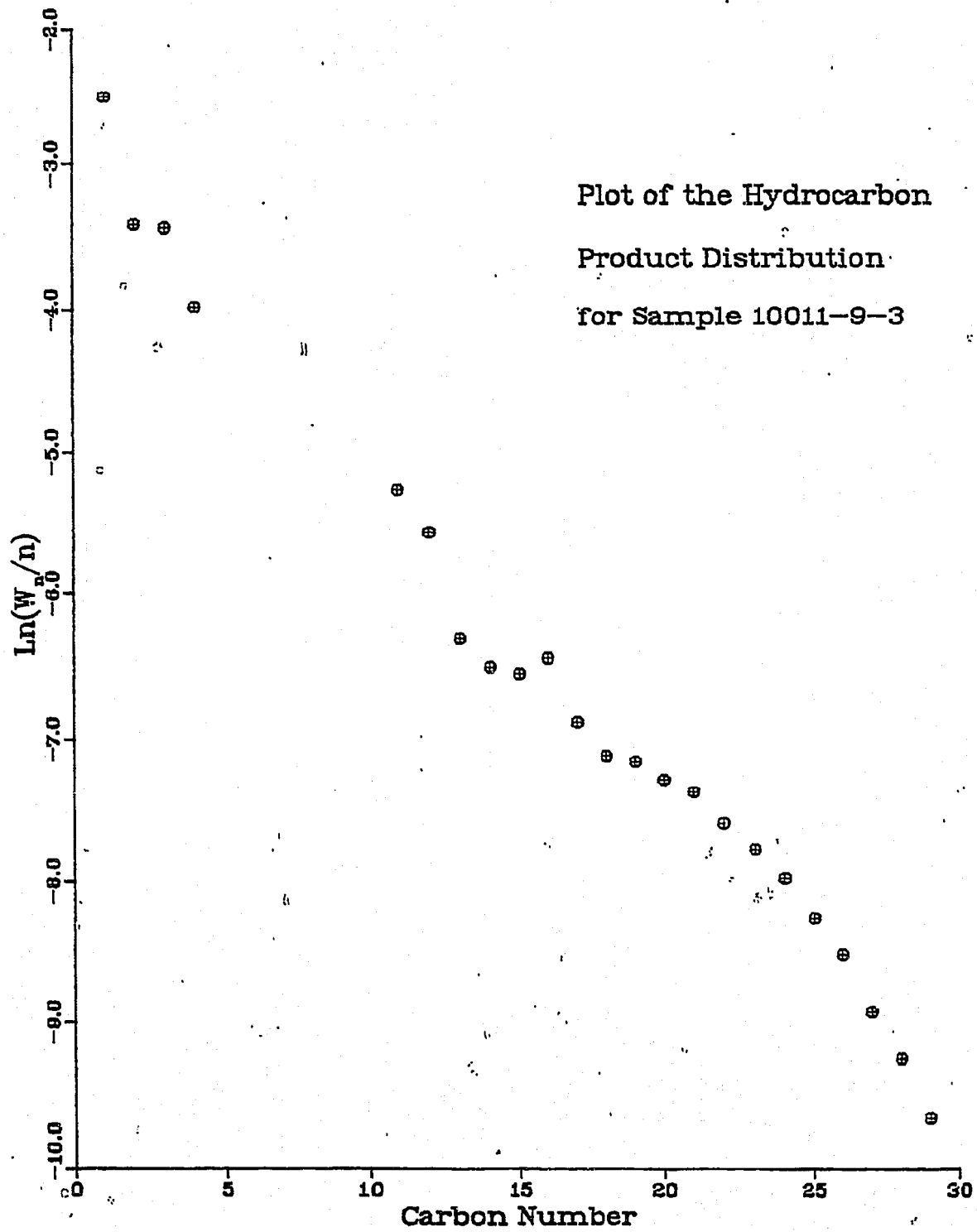
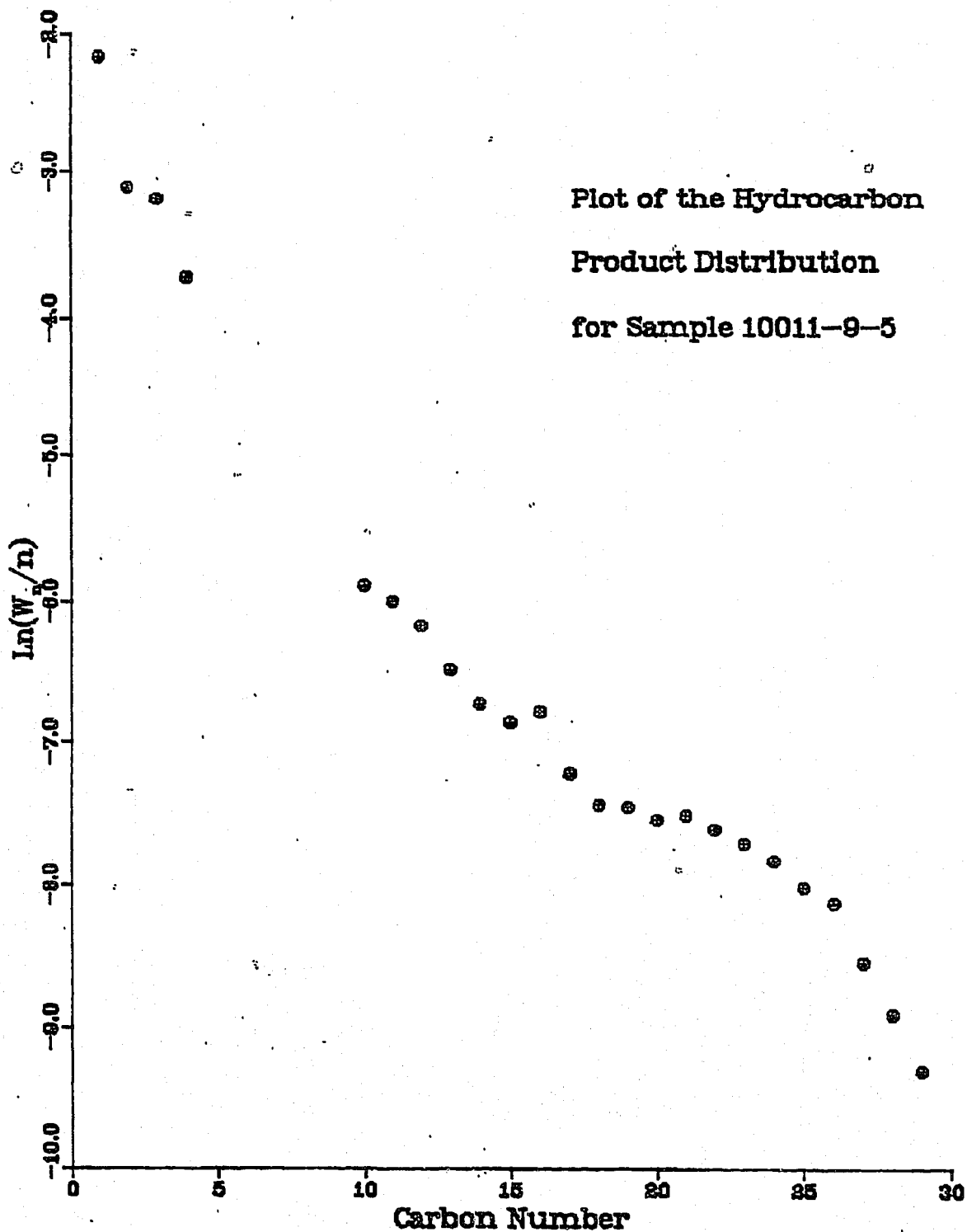


Figure 69



RUN 9972-11: UCC-201

The catalyst was 50% Fe precipitated on UCC-101. A different lot of this material was used in run 10011-7. The lot of material used in this run was the same used in run 10011-5, which was reported last quarter. That run used a high temperature hydrogen reduction as the activation step. This test was run parallel with run 10011-6. The activation procedure used was similar to the one used with the reference iron catalyst. The F-T synthesis condition was the same as the initial condition for the reference iron catalyst, and the reactor condition used in run 10011-5, 100PSIG, 250°C, 1:1 syngas.

The material balances, conversions, and hydrocarbon product selectivities of the five samples are given in table 12. The conversion and product selectivity are plotted as a function of time in figures 70 and 71. The material balances are almost all over 100% implying that the feed rate was actually higher than that calculated. The catalyst was run for only three days when, because of the poor conversion, the test was terminated.

The product selectivity was not that bad for an unpromoted catalyst but because of the poor conversion, the selectivity deserves no special discussion. As was seen in run 10011-7, increasing the pressure to 300P may have increased the conversion to a more reasonable level.

TABLE 12 RESULT OF SYNGAS OPERATION

RUN NO. 9972-11 CATALYST UCC-201 #9939-UB 80 CC 47.85GM (45.17 G AFTER THE RUN, 2.68GM) FEED H ₂ :CO:ARGON OF 50/50/0 @ 460 CC/MIN OR 345 GHSV					
RUN & SAMPLE NO.	9972-11-1	9972-11-2	9972-11-3	9972-11-4	9972-11-5
FEED H ₂ :CO:AR ₃	50:50:0	50:50:0	50:50:0	50:50:0	50:50:0
HRS ON STREAM	18.0	22.5	44.0	66.4	72.2
PRESSURE, PSIG	102	102	104	104	111
TEMP. C	252	252	252	252	250
FEED CC/MIN	460	460	460	460	460
HOURS FEEDING	17.813	4.5	31.5	22.417	5.833
EFFLNT GAS LITER	567.8	136.3	657.8	567.2	178.3
GM AQUEOUS LAYER	0.31	1.127	5.38	7.29	1.57
GM OIL	0.0	0.085	0.405	0.45	0.00
MATERIAL BALANCE					
GM ATOM CARBON %	116.42	110.97	113.75	93.17	111.47
GM ATOM HYDROGEN %	114.55	111.35	108.17	93.64	111.85
GM ATOM OXYGEN %	115.18	111.67	116.09	94.97	112.98
RATIO CH _x /(H ₂ O+CO ₂)	1.1620	0.9250	0.7627	0.8009	0.8514
RATIO X IN CH _x	2.4914	2.4791	2.5010	2.4334	2.4574
USAGE H ₂ /CO PRD _T	.2996	1.3654	1.2678	1.3552	1.3333
K EFFLNT SHIFT REACTN	0.77	0.50	0.53	0.44	0.56
CONVERSION %					
ON CO	10.60	10.77	9.80	10.87	10.92
ON H ₂	13.65	15.49	14.29	16.22	14.22
ON CO+H ₂	12.09	13.10	12.00	13.53	12.64
PRD _T SELECTIVITY, WT %					
CH ₄	14.63	14.27	15.61	12.95	13.66
C ₂ HC'S	12.14	11.84	11.13E	11.91	12.35
C ₃ H ₈	7.77	7.58	8.04	7.16	7.26
C ₃ H ₆	9.04	8.82	11.88	9.46	9.39
C ₄ H ₁₀	4.81	4.69	4.78	4.04	4.12
C ₄ H ₈	9.24	9.02	5.78	9.54	9.85
C ₅ H ₁₂	6.73	6.57	6.61E	4.54	4.52
C ₅ H ₁₀	0.84	0.82	1.06E	0.95	1.07
C ₆ H ₁₄	7.14	6.97	6.71	4.93	5.29
C ₆ H ₁₂ & CYCLO'S	0.89	0.87	1.53E	1.70	1.56
C ₇ + IN GAS	3.81	26.12	24.01	29.71	30.92
LIQ HC'S	0.00	2.42	2.84	3.12	0.00
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 C4	57.62	56.23	57.23	55.05	56.64
C5 @420 F	42.38	41.96	40.64	42.77	43.36
420-700 F	0.00	1.75	2.05	2.14	0.00
700-END PT	0.00	0.07	0.08	0.07	0.00
C5 -END PT	42.38	43.77	42.77	44.94	47.36
ISO/NORMAL MOLT RATIO					
C4	-	.7245	-	.1713	.1562
C5	-	1.1288	-	.3813	.3417
C6	-	2.3490	-	1.0529	1.2393
C4=	-	.0237	-	.0413	.0205
PARAFFIN/OLEFIN M RATIO					
C2	-	5.4974	-	5.5416	7.8597
C3	-	.8199	-	.7221	.7372
C4	-	.5020	-	.4089	.4038
C5	-	7.8056	-	4.6265	4.0989
LIQ HC COLLECTION -					
PHYS. APPEARANCE	TRACE OIL		TRACE OIL	TRACE OIL	TRACE OIL
DENSITY	-	-	-	-	-
N. REFRACTIVE INDEX	-	-	-	-	-
SIMULATED DISTILLATION					
10 WT % @ DEG F	---	---	377	371	---
16	---	---	400	394	---
50	---	---	475	472	---
84	---	---	555	571	---
90	---	---	590	607	---
RANGE(16-84 %)	---	---	155	178	---
WT % @420 F	---	---	25.0	29.0	---
WT % @700 F	---	---	97.1	97.6	---

Figure 70

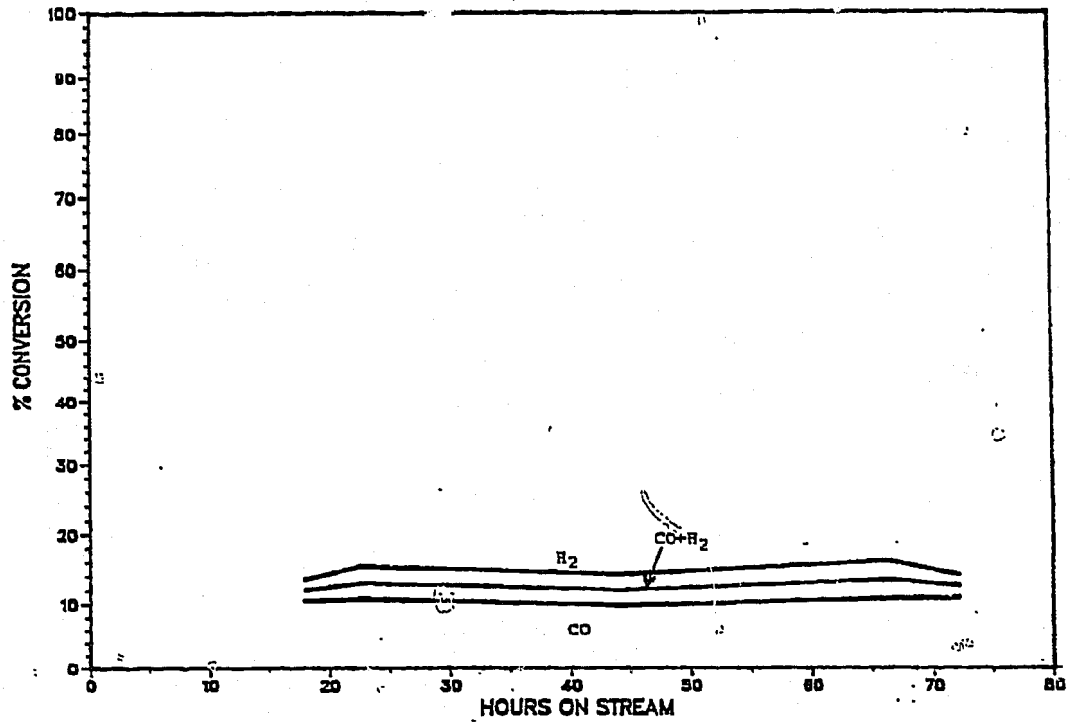
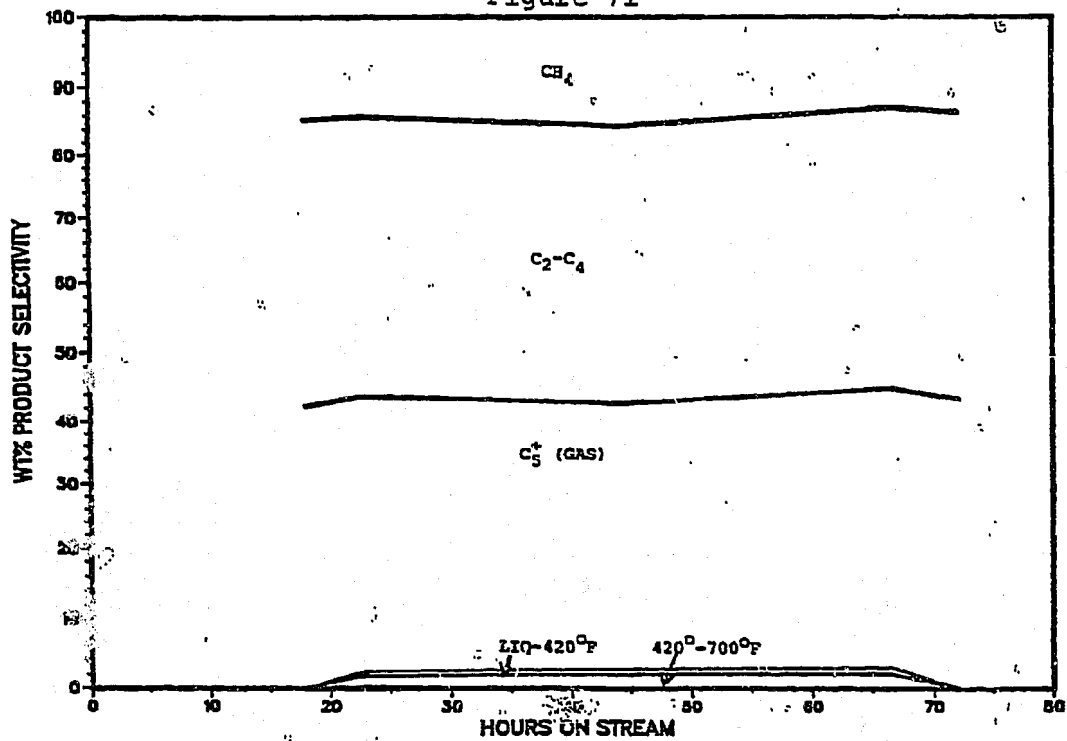


Figure 71



RUN 9972-12: Fe ON Y-52

The catalyst consisted of 20% iron oxide precipitated on sodium Y-52 zeolite. The activation used was similar to that used in runs 10011-6 and 9972-11 except that the initial CO treatment was done at pressure to better control the temperature in case of an exotherm. 2:1 syngas was used as feed since the catalyst had not been promoted and was not expected to have significant water gas shift activity. The temperature was raised from 250°C to 280°C after four days on stream in an attempt to increase conversion.

The material balances, conversions, and hydrocarbon product selectivities are given in tables 13A to 13C. Figures 72 and 73 show the conversion and product selectivity as functions of time on stream. The simulated distillation of two representative samples #4 and #11 are shown in figures 74 and 75. Figures 76 and 77 show the product distributions in a Schultz-Flory format. The material balances were all high again implying that the feed rate was higher than expected. If that was the case, the only calculation affected was the material balance. The conversion and selectivity were not affected by this error. Only sample #5 is suspect with the actual balance on hydrogen being 37% higher than the balance on carbon. That sample is best ignored, but the rest should be accurate. The conversion of syngas was about twice that obtained with the previous catalyst. Similar weights of both catalysts were loaded into the reactor but this formulation contained only 20% iron oxide while the catalyst from the previous run was ~50% iron oxide. On an iron basis this catalyst was five times more active than the last. The H₂:CO usage ratio of 1:4 showed that the catalyst actually had some W.G.S. activity. At 250°C approximately 25% of the converted CO became CO₂. When the reactor temperature was raised to 280°C the conversion did not increase significantly and quickly dropped back to the level it was at 250°C. This behavior is a sign of catalyst deactivation. Even though the hydrogen content of the hydrocarbons increased with the increasing temperature, the usage ratio actually decreased. The water gas shift activity increased with respect

to the F-T synthesis activity. At 280°C approximately 35% of the CO converted became CO₂. The source of this WGS activity must have been the migration of the sodium from the Y zeolite out into the iron. While sodium is not as good a promoter as potassium, it is effective.

The product selectivity again had some good and some bad characteristics. At 250°C, the methane selectivity was ~14%. This was not too bad for an unpromoted catalyst with 2:1 syngas feed. At 280°C the methane selectivity almost doubled to ~25%. This was poor even for the unpromoted catalyst. Analysis of the other gaseous hydrocarbons showed the product from this catalyst to be intermediate between those of the reference iron catalyst and those of the other molecular sieve containing catalysts. Both the paraffin-olefin ratio of the C₃ and C₄ hydrocarbons and the iso/normal ratio of C₄, C₅, and C₆ paraffins were between the values for the two types of catalysts. What was impressive about the product distribution was that at 250°C with 2:1 syngas feed up to 50% of the hydrocarbons were in the gasoline range. This was also seen in run 10011-7, another unpromoted catalyst at 280°C and 1:1 syngas feed. In addition, with this catalyst there was more product boiling in the diesel fuel range.

Looking at the product distribution in a Schultz-Flory format exposed some unusual features of the catalytic activity. The low temperature sample, #4, shows marked deviations from a straight line. In the high temperature samples this deviation became so great that the product distribution curve was almost S shaped. For sample #11 the product distribution was almost flat for C₁₈-C₂₇. The concentration only dropped 5% from C₁₈ to C₂₇. In sample #4 the concentration of C₂₇ was only 30% that of C₁₈. If the rest of the product distribution also fit two straight lines, this sample would look like one from run 10011-6 with a double α . The second α would be close to 1.0. It is concluded that this product did not fit a Schultz-Flory distribution.

This catalyst performed well in producing gasoline range products. Since the isomerization ability was better than that of conventional F-T catalysts, the gasoline product quality should be slightly improved but not as much as the products from the other molecular sieve containing catalysts which had higher isomerization activity.

TABLE 13A RESULT OF SYNGAS OPERATION

RUN NO. 9972-12						
CATALYST 20%FE-Y52 #9939-85 80CC 44.63GM(17.11G AFTER THE RUN, +2.48GM)						
FEED H ₂ :CO:ARGON OF 60/30/10 @ 400 CC/MIN OR 300 GHSV						
RUN & SAMPLE NO.	9972-12-1	9972-12-2	9972-12-3	9972-12-4	9972-12-5	
FEED H ₂ :CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10	
HRS ON STREAM	21.5	26.7	46.1	51.4	71.2	
PRESSURE, PSIG	100	101	95	95	97	
TEMP. °C	251	251	251	251	251	
FEED CC/MIN	400	400	400	400	400	
HOURS FEEDING	21.4167	5.333	19.4167	5.25	19.75	
EFFLUENT GAS LITER	552.6	130.8	482.8	131.9	505.3	
GM AQUEOUS LAYER	15.77	5.14	19.47	4.41	16.33	
GM OIL	1.44	0.77	2.91	1.07	3.86	
MATERIAL BALANCE						
GM ATOM CARBON %	112.79	113.66	104.51	108.96	93.67	
GM ATOM HYDROGEN %	117.43	112.72	116.56	115.64	128.50	
GM ATOM OXYGEN %	116.78	119.10	113.80	114.04	97.50	
RATIO CH ₄ /(H ₂ O+CO ₂)	0.8579	0.9267	0.7077	0.8232	0.8612	
RATIO X IN CH ₄	2.4093	2.3700	2.3910	2.3605	2.4298	
USAGE H ₂ /CO PRODT	1.3639	1.4255	1.4139	1.4148	1.5058	
K EFFLUENT SHIFT REACTN.	1.13	0.85	0.89	0.93	1.15	
CONVERSION %						
ON CO	29.48	30.55	29.58	29.17	33.00	
ON H ₂	20.47	23.68	21.57	21.00	19.23	
ON CO+H ₂	23.39	25.98	24.05	23.61	22.91	
PRDT SELECTIVITY, WT %						
CH ₄	14.91	13.53	14.43	13.23	15.65	
C ₂ HC'S	8.47	7.83	8.34	7.78	8.19	
C ₃ H ₈	4.02	4.26	4.20	3.92	5.27	
C ₃ H ₆	5.51	7.05	7.18	7.08	6.48	
C ₄ H ₁₀	3.70	2.67	2.61	2.55	3.20	
C ₄ H ₈	11.20	7.35	7.42	7.41	6.93	
C ₅ H ₁₂	3.52	3.20	3.06	3.15	3.44	
C ₅ H ₁₀	1.18	1.20	1.34	1.38	1.27	
C ₆ H ₁₄	4.09	3.63	3.53	3.33	3.65	
C ₆ H ₁₂ & CYCLO'S	2.15	2.02	2.05	1.83	1.73	
C ₇ + IN GAS	35.18	35.27	31.46	29.70	26.49	
LIQ HC'S	6.01	12.03	14.38	18.63	17.68	
TOTAL	100	100	100	100	100	

SUBGROUPING						
C1 -C4	47.88	42.66	44.18	41.97	45.74	
C5 -420 F	48.65	50.00	47.39	45.79	45.65	
420-700 F	3.36	7.01	7.88	10.08	6.19	
700-END PT	0.11	0.32	0.55	2.16	2.42	
C5 -END PT	52.12	57.34	56.82	58.07	54.26	
ISO/NORMAL MOLE RATIO						
C4	.1151	.0816	.0675	.0585	.0601	
C5	.1435	.1185	.0942	.1137	.0971	
C6	.6525	.5163	.5265	.5529	.3156	
C4-	.1156	.0692	.0690	.0750	.0715	
PARAFFIN/OLEFIN M RATIO						
C2	4.7824	4.2471	4.7031	4.2242	8.2331	
C3	.6956	.5761	.5589	.5280	.7763	
C4	.3241	.3501	.3403	.3326	.4451	
C5	2.8939	2.5665	2.2234	2.2103	2.6389	
LJO HC COLLECTION						
PHYS. APPEARANCE						
DENSITY						
N. REFRACTIVE INDEX						
SIMULATED DISTILLATION						
10 WT % @ DEG F	330	337	332	340	282	
16	345	364	344	375	293	
50	445	454	449	480	407	
84	569	589	573	666	684	
90	607	628	644	715	728	
RANGE (16-84 %)	224	225	229	291	391	
WT % @420 F	42.2	39.0	41.4	34.3	51.3	
WT % @700 F	98.2	97.3	96.2	88.4	86.3	

TABLE 13B RESULT OF SYNGAS OPERATION

RUN NO. 9972-12
 CATALYST 20%FE-Y52 #9939-85 BOCC 44.63GM(47.11G AFTER THE RUN,+2.48GM)
 FEED H2:CO:ARGON OF 60/30/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO..	9972-12-6	9972-12-7	9972-12-8	9972-12-9	9972-12-10
FEED H2:CO:AR	60:30:10	60:30:10	60:30:10	60:30:10	60:30:10
HRS ON STREAM	77.2	94.4	101.4	119.2	125.0
PRESSURE, PSIG	98	97	94	100	99
TEMP. C	251	250	280	280	280
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	6.0833	17.1667	7.0	17.75	5.75
EFFLNT GAS LITER	157.8	450.1	178.8	466.4	152.2
GM AQUEOUS LAYER	4.37	11.82	2.7	5.92	2.106
GM OIL	0.96	2.59	0.93	1.15	0.34
MATERIAL BALANCE					
GM ATOM CARBON %	107.73	111.54	115.96	113.40	116.88
GM ATOM HYDROGEN %	120.08	116.46	117.22	117.30	119.94
GM ATOM OXYGEN %	111.05	117.51	117.53	116.24	116.88
RATIO CHX/(H2O+CO2)	0.8721	0.7602	0.9479	0.8912	0.9999
RATIO X IN CHX	2.3671	2.3739	2.7079	2.7880	2.6943
USAGE H2/CO PRDPT	1.4434	1.4278	1.1055	1.1540	1.2072
K EFFLNT SHIFT REACTN	0.97	0.81	3.40	2.86	2.66
CONVERSION %					
ON CO	27.74	22.91	39.58	32.83	34.27
ON H2	18.96	17.50	22.01	19.01	20.16
ON CO+H2	21.68	19.25	27.83	23.52	24.78
PRDPT SELECTIVITY, WT %					
CH4	13.45	13.81	24.62	27.83	24.76
C2 HC'S	12.96	7.68	13.91	13.85	12.67
C3H8	4.37	4.17	10.98	11.58	10.07
C3H6	6.72	7.14	5.01	5.51	4.93
C4H10	2.75	2.66	5.21	5.62	5.03
C4H8	6.99	7.40	5.66	6.23	5.34
C5H12	3.06	2.96	4.24	4.85	4.26
C5H10	1.36	1.44	0.51	0.59	0.47
C6H14	3.24	3.63	4.06	4.22	3.93
C6H12 & CYCLO'S	1.78	1.83	1.03	1.00	0.93
C7+ IN GAS	28.27	30.04	14.95	12.85	22.87
LIO HC'S	15.07	17.23	9.81	5.85	4.73
TOTAL	100	100	100	100	100

SUBGROUPING					
C1 - C4	47.23	42.87	65.40	70.53	62.80
C5 - 120 F	42.31	47.18	26.92	34.71	33.49
120-700 F	7.93	7.54	5.23	2.98	2.44
700-END PT	2.53	2.41	2.45	1.68	1.28
C5 -END PT	52.77	57.13	34.40	29.37	27.20
ISO/NORMAL MOLE RATIO					
C4	.0650	.0625	.1157	.0982	.0970
C5	.0814	.0984	.2110	.1875	.1728
C6	.3225	.4892	.8962	.7172	.6851
C4+	.0708	.0696	.1100	.0961	.0939
PARAFFIN/OLEFIN M RATIO					
C2	.8813	1.6240	9.5434	32.5143	13.6707
C3	.6202	.5567	2.0932	2.0053	1.9482
C4	.3793	.3476	.8885	.8716	.9086
C5	2.1915	1.9941	8.0860	8.0471	8.7273
LIQ HC COLLECTION					
PHYS. APPEARANCE					
DENSITY					
N. REFRACTIVE INDEX					
SIMULATED DISTILLATION					
10 WT % @ DEG F	343	337	379	384	NO
16	382	345	404	407	
50	504	446	551	571	HTQ-
84	705	685	749	760	
90	746	732	784	792	UID
RANGE (16-84 %)	323	340	345	353	
WT % @120 F	30.6	42.2	21.7	20.2	
WT % @700 F	83.2	86.0	75.0	71.2	

TABLE 13C RESULT OF SYNGAS OPERATION

RUN NO. 9972 12
 CATALYST ROFFE-Y52 #9939-85 80CC 44.63GM(47.11G AFTER THE RUN, +2.48GM)
 FEED H₂:CO:ARGON OF 60/30/10 @ 400 CC/MIN OR 300 GHSV

RUN & SAMPLE NO. 9972-12-11 9972-12-12

	60:30:10	60:30:10
FEED H ₂ :CO:AR	60:30:10	60:30:10
HRS ON STREAM	141.6	165.8
PRESSURE.PSIG	100	104
TEMP. C	280	280
FEED CC/MIN	400	400
HOURS FEEDING	16.5837	24.1667
EFFLNT GAS LITER	440.6	644.9
GM AQUEOUS LAYER	6.074	9.44
GM OIL	0.98	0.85

MATERIAL BALANCE

GM ATOM CARBON %	114.62	115.47
GM ATOM HYDROGEN %	117.20	118.70
GM ATOM OXYGEN %	118.71	117.80
RATIO CHX/(H ₂ O+CO ₂)	0.8427	0.9070
RATIO X IN CHX	2.7144	2.7721
USAGE H ₂ /CO PRQDT	1.1444	1.2500
K EFFLNT SHIFT REACTN	2.49	2.14

CONVERSION %

ON CO	30.65	30.07
ON H ₂	18.15	18.90
ON CO+H ₂	22.25	22.56

PRDT SELECTIVITY.WT %

CH ₄	23.30	27.32
C ₂ HC'S	15.11	13.58
C ₃ H ₈	11.77	11.04
C ₃ H ₆	5.84	6.65
C ₄ H ₁₀	5.99	6.27
C ₄ H ₈	6.67	6.94
C ₅ H ₁₂	5.24	5.21
C ₅ H ₁₀	0.57	0.73
C ₆ H ₁₄	4.72	4.44
C ₆ H ₁₂ & CYCLO'S	2.92	1.09
C ₇ IN GAS	12.18	13.48
LIQ HC'S	5.69	3.24

TOTAL	100	100
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SUBGROUPING		
C1 -C4	68.68	71.81
C5 -420 F	26.85	25.70
420 700 F	2.93	1.90
700-END PT	1.54	0.59
C5 --END PT	31.32	28.19
ISO/NORMAL MOLE RATIO		
C4	.0868	.1146
C5	.1489	.1489
C6	.6151	.5962
C4 =	.0957	.1075
PARAFFIN/OLEFIN M RATIO		
C2	14.3681	13.4708
C3	1.9222	1.5847
C4	.8677	.8717
C5	8.9342	6.9608
LIQ HC COLLECTION		
PHYS. APPEARANCE		
DENSITY		
N. REFRACTIVE INDEX		
SIMULATED DISTILLATION		
10 WT % @ DEG F	383	383
16	405	403
50	538	513
84	766	724
90	802	773
RANGE (16-84 %)	361	321
WT % @420 F	21.5	23.2
WT % @700 F	73.0	81.1

RUN NO. 9972-12

Figure 72

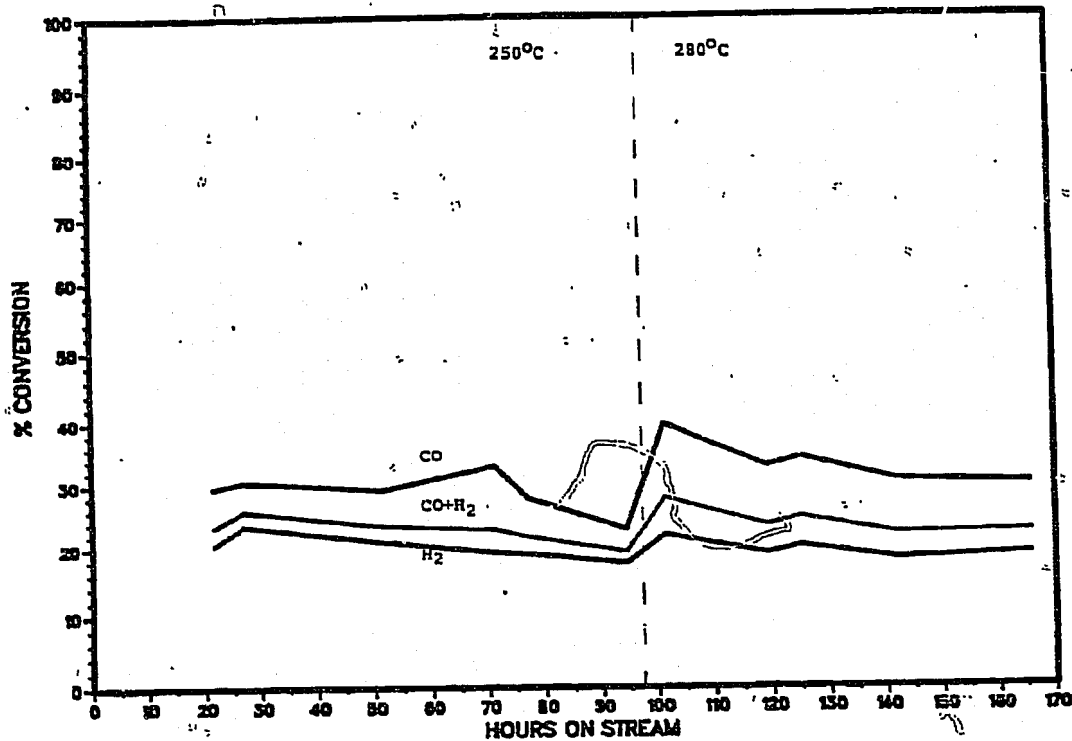


Figure 73

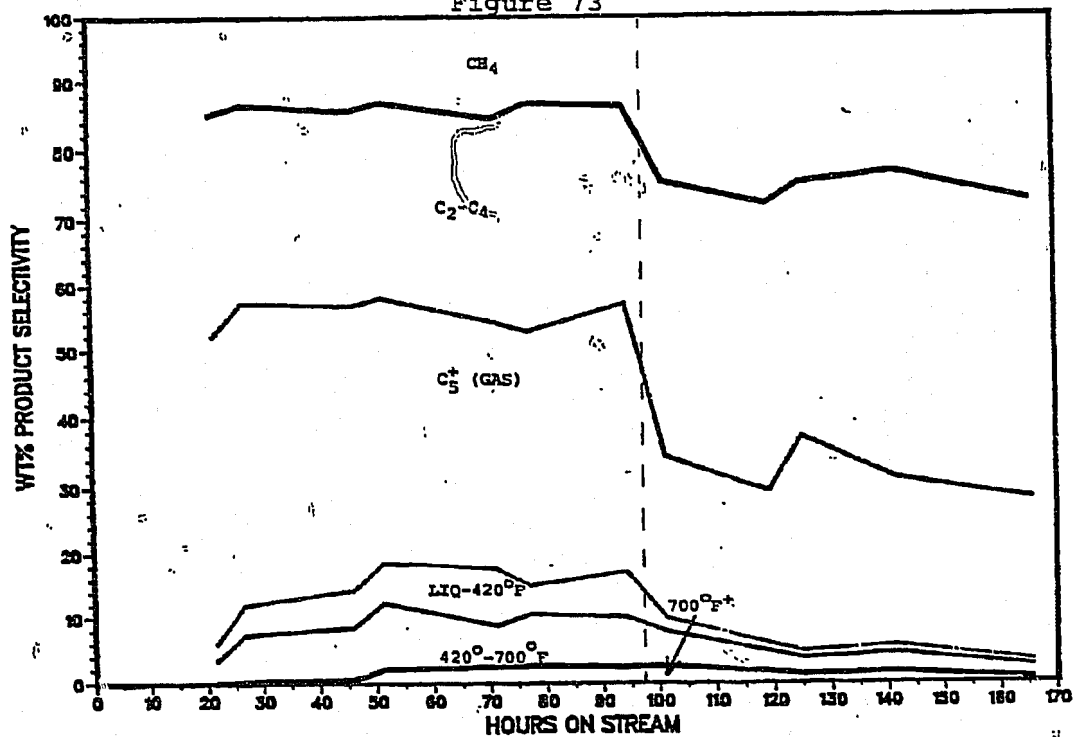
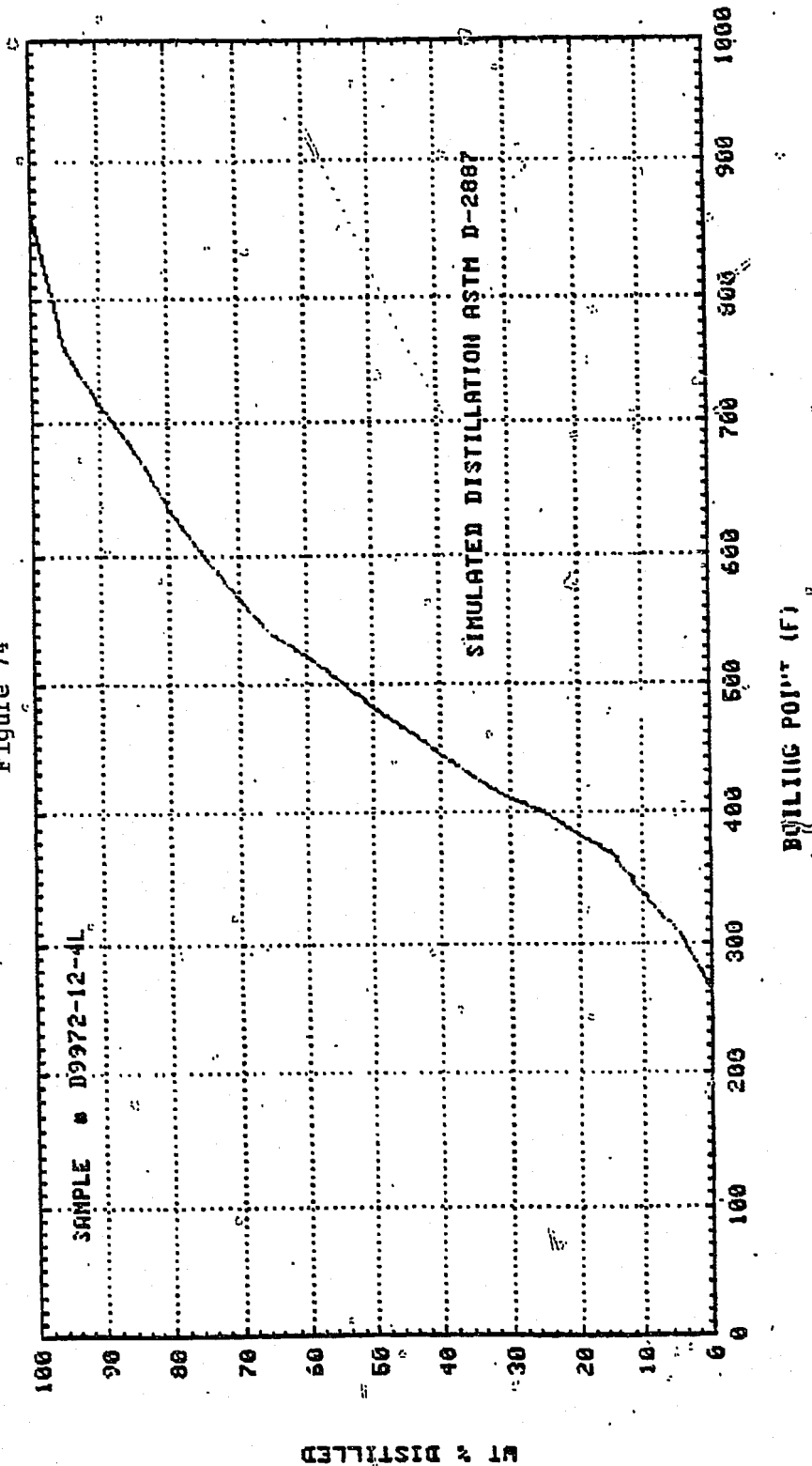
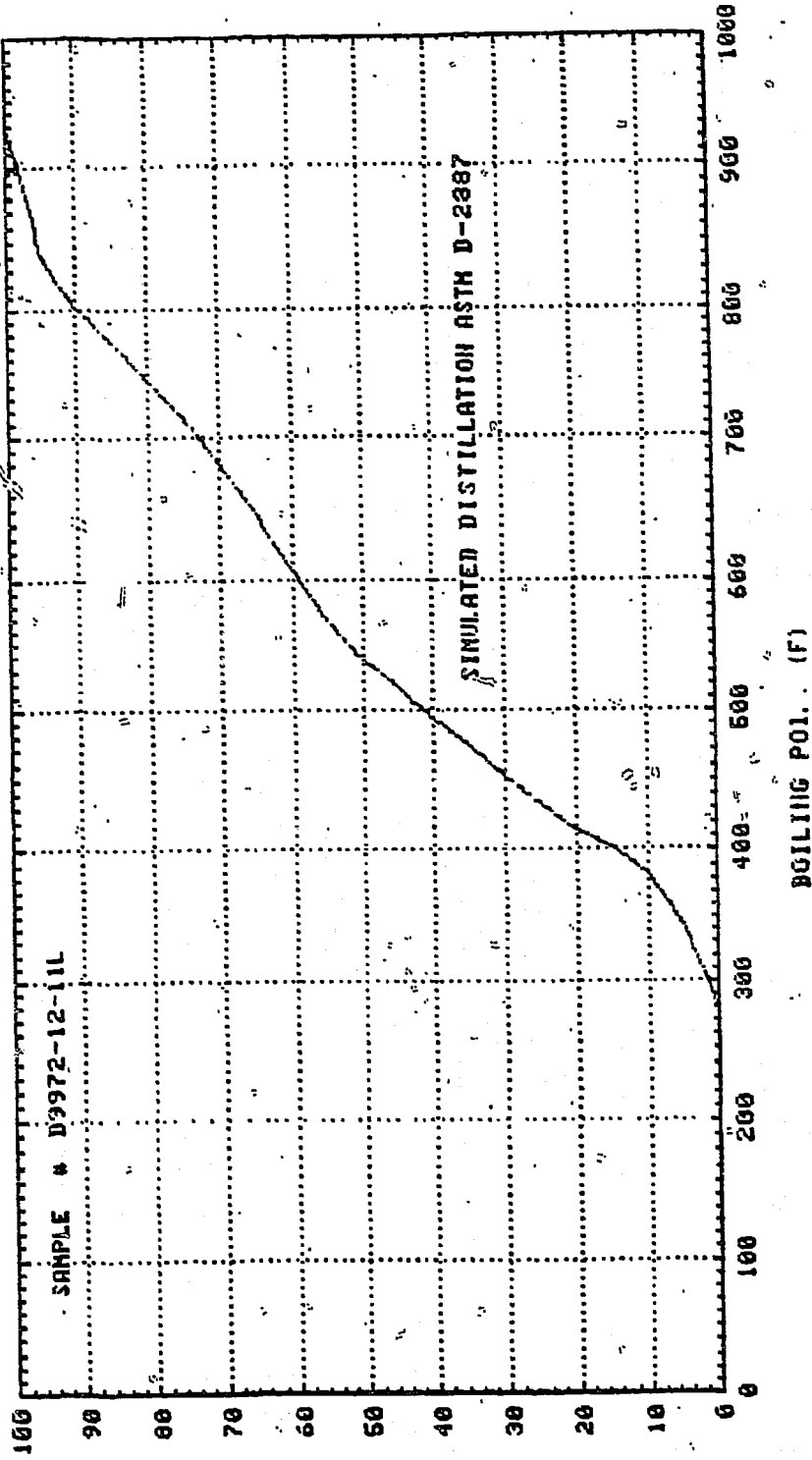


Figure 74



WT % DISTILLED

Figure 75



WT % DISTILLED

Figure 76

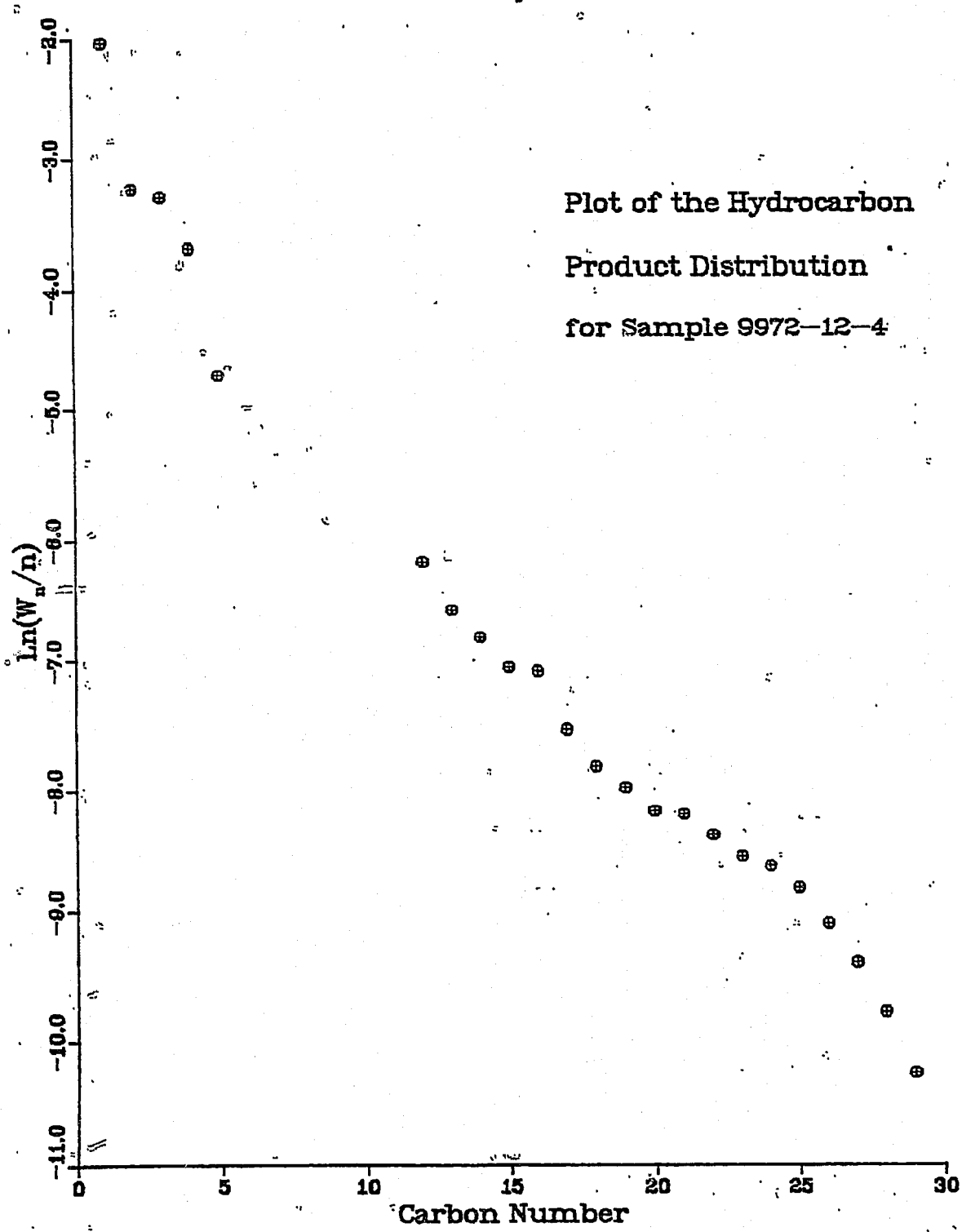
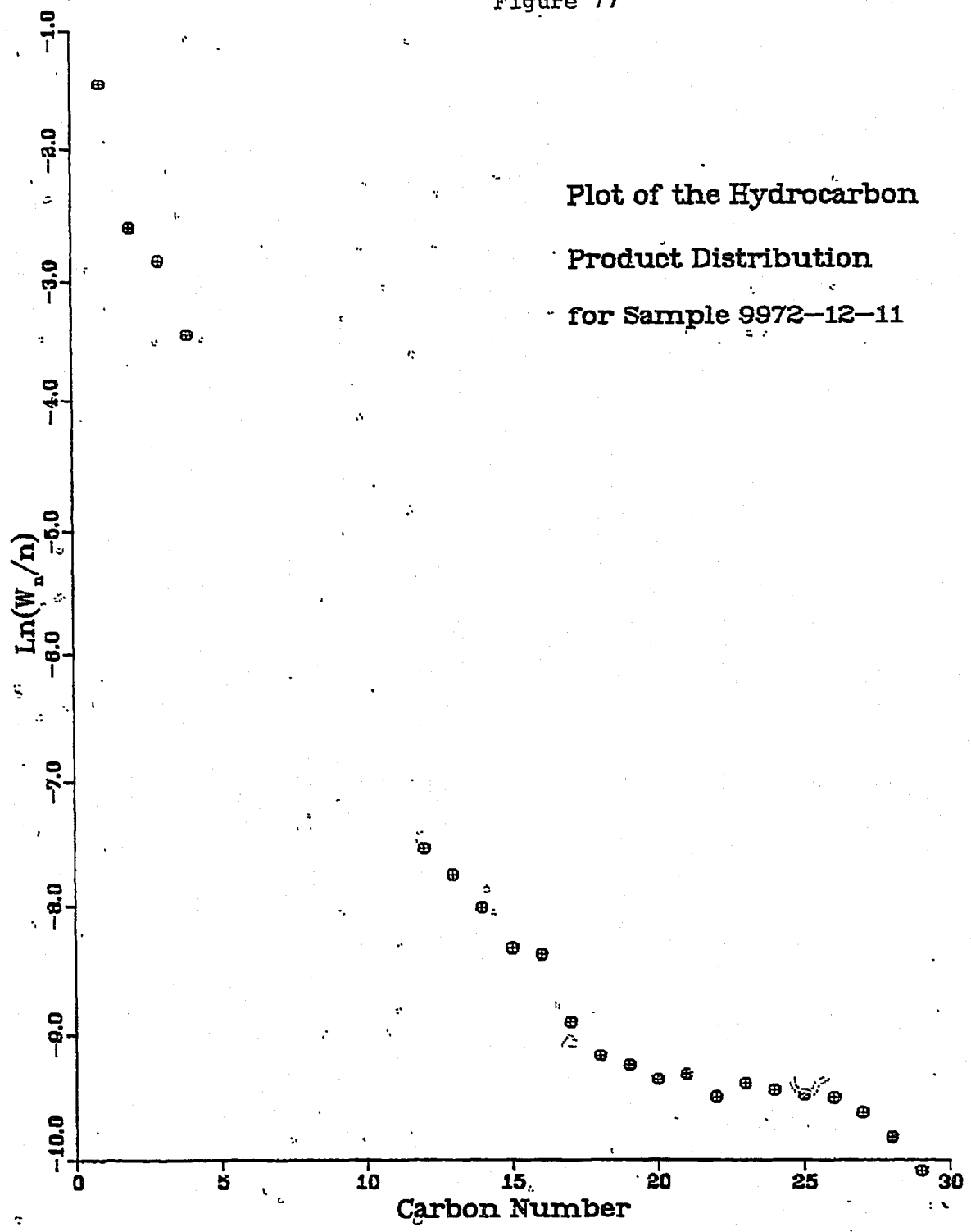


Figure 77



SUMMARY OF TASK 2 RESULTS

Following last quarter's preliminary catalyst screening, this quarter's syngas testing led to substantial progress. By this time a reliable activation procedure was established. A state of the art reference catalyst was fully evaluated. The results of that test were used to establish performance criteria. A number of molecular sieve containing catalysts were tested. The results of those tests showed the beneficial effects of the molecular sieve component. While none of the catalysts tested so far produced more condensed product, several showed significantly superior quality of the fuel product.

The reference catalyst had an initial loss of activity followed by quite stable operation. The catalyst showed high syngas conversion and low selectivity to methane. Under almost all conditions tested, the catalyst produced a wax containing liquid product. Even under conditions which had poor selectivity to C_5^+ products and high gas production, the condensed product was solid. The products were mainly straight chain olefins. The hydrocarbon products exhibited a Schultz-Flory distribution with a double α that is, the C_{20}^+ hydrocarbons were in higher concentration that would be predicted from the C_1 - C_{19} hydrocarbon product distribution.

The physical mixtures of promoted unsupported iron and UCC-101 had improved product distributions with the exception of methane which was always higher than that of the reference catalyst under similar conditions. Operating conditions could be selected to keep the methane level acceptable, <10wt%. One physical mixture catalyst had very good selectivity to gasoline, 50%, and total motor fuels, 70%, at 220°C. The catalyst did pay the price for this superior selectivity with low conversion and some deactivation. The other physical mixture catalyst had one sample with similar good selectivity but that catalyst did not consistently show good product selectivity. The products from both catalysts were more isomerized and less olefinic (more saturated

than those of the reference catalyst. This would result in important improvements, both in gasoline octane and diesel and turbine fuel pour point. These catalysts produced liquids, not solid condensed product. The SSC containing catalysts produced less very heavy hydrocarbons than the reference catalyst. Furthermore, the catalysts also showed signs of a carbon number cut off in the product at the end of the liquid fuel range even at low reaction temperatures.

The two unpromoted catalysts, as expected, did not have as favorable a product distribution as the promoted catalysts. Both produced up to 50% gasoline under various conditions. However, the selectivity to total motor fuel was not as impressive. The iron on sodium Y catalyst saw sodium migration from the zeolite to the iron imparting water gas shift activity to the catalyst.

The catalyst testing in Task #2 went well this quarter. The testing next quarter will continue along similar lines of attack. Molecular sieves will be iron loaded by physical mixture, precipitation and occlusion techniques. All of these iron catalysts will be potassium promoted. Cobalt loaded molecular sieves will also be studied next quarter. Some of these catalysts will be promoted with thorium.

APPENDIX D : SURFACE STUDIES

The purpose of our studies is to synthesize and evaluate new catalysts that produce olefins or other molecules from carbon monoxide and hydrogen. The new catalysts that were studied in this quarter included thorium oxide, ThO_2 , and various rhodium compounds: Rh, Rh_2O_3 and Na_2RhO_3 .

1) Thorium Oxide

These studies are being carried out in the Lawrence Livermore Laboratory where there are extensive facilities for handling actinide elements and their compounds, that include thorium oxide. High surface area oxide was synthesized by precipitating thorium carbonate and then heating slowly up to 400°C . CO_2 and H_2O are driven off and oxide is produced with a surface area of about $10 \text{ m}^2/\text{gm}$.

2) Rhodium Compounds

Many runs have been completed in this exploratory phase of carbon monoxide hydrogenation on rhodium foil and rhodium oxide samples. The initial reaction rates and product distributions obtained are summarized in the following table:

Sample	Rhfoil	Rh_2O_3	Na_2RhO_3
CO:H ₂ Ratio	3:1	1:1	2:1
Total Pressure (atm)	6	6	6
(at 300°C) Turnover Frequency CH ₄	.15	$\sim 10^{-3}$	1.57×10^{-3} *
wt% CH ₄	90	29	64
C ₂	7	22	19
C ₃ +	3	25	~ 15
Oxygenates	---	19 (initial rate)	~ 2

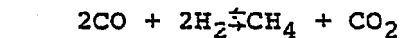
* Turnover frequency calculated by assuming all of oxide is surface oxide.

We have found an inverse deuterium isotope effect on the rhodium foil, similar to that found on ruthenium by Kenner and Bell (J. Cat. 67, 175-185 (1981)), with Rate (D₂):Rate (H₂) = 1.4. Also, the partial pressure dependence of the reactants has been determined. Assuming a rate law of the form $\text{Rate} = K \frac{P_{\text{CO}}^X P_{\text{H}_2}^Y}{P_{\text{CO}} P_{\text{H}_2}}$, the values X = -1 and Y = +1 were obtained. Activation energies for different total pressure and different partial pressures of the reactant gases were calculated, and an interesting result was obtained. The activation energy did not depend on the total pressure of the reactant gases, but changed with the CO to H₂ partial pressure ratio. The results are shown in the table below:

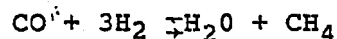
Rhfoil

CO:H ₂ ratio	2:1	1:2	1:2
Total Pressure (atm)	6	6	1
E _a (Kcal/mol)	22.5	18	18
Rate (D ₂):Rate (H ₂) (at 300°)	1.3	1.4	--

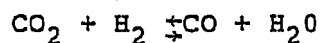
Future work on rhodium foils includes studying the effect of adding CO₂ and H₂O to reaction gas mixtures, aiming to explain the change in activation energy by relating the following two possible methanation reaction pathways



and



through the water gas shift reaction



P

Also we are planning to look for catalytic oxides which have a strong enough lattice to maintain the oxidation state of the active metal center under the reducing environment of the reaction. This work will include X ray photoelectron spectroscopy, auger electron spectroscopy and thermal desorption, before and after each run, to see if the integrity of the catalyst surface is maintained during the reaction. Oxides which have been prepared for this purpose include Na_2RhO_3 , TiRhO_3 , Sr_4RhO_6 , FeRhO_3 and CuRh_2O_4 .