Table 17

RESULT OF SYNGAS OPERATION

RUN NO. 11723-12
CATALYST HiCoThU103+U101+CuZnAl2O3 250CC 120 GM (167 AFTER RUN +47 G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11723-12-11	723-12-12	723-12-13	723-12-14	723-12-15
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	123.5	142.0	146.5	165.0	173.0
PRESSURE,PSIG	299	301	302	302	302
TEMP. C	265	265	265	265	264
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	6.50	25.00	4.50	23.00	8.00
EFFLNT GAS LITER	253.65	991.50	181.95	943.55	333.50
GM AQUEOUS LAYER	53.03	203.95	35.58	181.84	60.44
GM OIL	21.97	84.51	14.63	74.79	23.93
MATERIAL BALANCE					
GM ATOM CARBON %	94.65	94.66	95.84	95.18	92.96
GM ATOM HYDROGEN %	98.39	99.66	98.81	99.46	99.92
GM ATOM OXYGEN %	98.06	98.31	98.85	99.03	96.68
RATIO CHX/(H2O+CO2)	0.9015	0.8945	0.9104	0.8852	0.8848
RATIO X IN CHX	2.3544	2.3617	2.3646	2.3739	2.3894
USAGE H2/CO PRODT	1.9536	1.9632	1.9577	1.9859	1.9851
FEED H2/CO FRM EFFLNT	1.0395	1.0528	1.0310	1.0449	1.0750
RESIDUAL H2/CO RATIO	0.5105	0.5314	0.5234	0.5454	0.6007
RATIO CO2/(H2O+CO2)	0.1016	0.1013	0.0994	0.0980	0.1007
K SHIFT IN EFFLNT	0.0577	0.0599	0.0578	0.0593	0.0673
SPECIFIC ACTIVITY SA	1.0798	1.0025	0.9839	0.9029	0.8086
CONVERSION					
ON CO %	36.66	36.41	35.39	34.68	34.26
ON H2 %	68.89	67.90	67.20	65.91	63.26
ON CO+H2 %	53.09	52.56	51.54	50.63	49.28
PRDT SELECTIVITY,WT %					
CH4	15.21	15.85	15.86	16.50	17.11
C2 HC'S	2.47	2.42	2.46	2.45	2.61
C3H8	3.35	3.18	3.43	3.09	3.32
C3H6=	2.04	1.87	2.28	1.77	1.85
C4H10	2.87	2.47	2.54	2.51	2.61
C4H8=	3.62	3.40	3.27	3.11	3.20
C5H12	2.92	2.68	2.77	2.68	2.92
C5H10=	4.23	4.00	4.17	3.75	3.70
C6H14	3.00	3.03	3.21	2.99	3.11
C6H12= & CYCLO'S	3.27	3.20	3.31	3.25	3.07
C7+ IN GAS	8.59	9.12	9.22	9.05	9.85
LIQ HC'S	48.45	48.77	47.49	48.84	46.65
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 17 (continued)

SUB-GROUPING					
C1 -C4	29.55	29.19	29.83	29.44	30.71
C5 -420 F	45.31	45.50	45.57	45.26	44.56
420-700 F	20.60	20.74	19.96	20.53	20.06
700-END PT	4.54	4.57	4.64	4.77	4.67
C5+-END PT	70.45	70.81	70.17	70.56	69.29
ISO/NORMAL MOLE RATIO					
C4	0.0922	0.0560	0.0692	0.0552	0.0527
C5	0.0904	0.0743	0.0781	0.0749	0.0771
C6	0.2062	0.1949	0.1907	0.1653	0.1775
C4=	0.0849	0.0727	0.0658	0.0694	0.0721
PARAFFIN/OLEFIN RATIO					
C3	1.5705	1.6270	1.4380	1.6632	1.7110
C4	0.7659	0.7023	0.7492	0.7768	0.7859
C5	0.6716	0.6529	0.6462	0.6963	0.7681
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8265		0.8275	
RATIO CH4/(1-A)**2		5.2669		5.5452	
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL/SLD		OIL/SLD	
DENSITY		0.7573		0.7572	
N, REFRACTIVE INDEX		1.4264		1.4264	
SIMULT'D DISTILATN					
10 WT % @ DEG F		273		278	
16		302		303	
50		433		433	
84		637		639	
90		695		697	
RANGE(16-84 %)		335		336	
WT % @ 420 F	48.11	48.11	48.20	48.20	47.00
WT % @ 700 F	90.63	90.63	90.23	90.23	90.00

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Table 18

RESULT OF SYNGAS OPERATION

RUN NO. 11723-12
CATALYST HiCoThU103+U101+CuZnA1203 250CC 120 GM (167 AFTER RUN +47 G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11723-12-16	723-12-17	723-12-18	723-12-19	723-12-20
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	189.5	196.3	213.5	220.0	237.5
PRESSURE,PSIG	297	299	297	297	300
TEMP. C	265	265	264	265	265
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	24.50	6.83	24.00	6.50	24.00
EFFLNT GAS LITER	1024.00	284.65	1023.70	274.90	1028.00
GM AQUEOUS LAYER	185.09	51.66	181.45	48.22	178.03
GM OIL	73.29	19.61	68.86	17.92	66.15
MATERIAL BALANCE					
GM ATOM CARBON %	93.89	93.41	94.29	93.89	93.54
GM ATOM HYDROGEN %	99.79	99.04	101.13	99.08	100.56
GM ATOM OXYGEN %	97.13	97.14	97.85	97.44	97.25
RATIO CHX/(H2O+CO2)	0.8991	0.8841	0.8895	0.8881	0.8830
RATIO X IN CHX	2.3842	2.3907	2.3982	2.4028	2.4120
USAGE H2/CO PRODT	1.9877	1.9982	2.0025	1.9997	2.0102
FEED H2/CO FRM EFFLNT	1.0628	1.0603	1.0725	1.0552	1.0751
RESIDUAL H2/CO RATIO	0.5859	0.5814	0.6018	0.5851	0.6111
RATIO CO2/(H2O+CO2)	0.0953	0.0968	0.0950	0.0970	0.0963
K SHIFT IN EFFLNT	0.0617	0.0623	0.0632	0.0629	0.0651
SPECIFIC ACTIVITY SA	0.8083	0.8010	0.8054	0.7844	0.7241
CONVERSION					
ON CO %	34.02	33.80	33.60	33.23	33.16
ON H2 %	63.63	63.70	62.74	62.98	62.01
ON CO+H2 %	49.27	49.19	48.68	48.50	48.11
PRDT SELECTIVITY,WT %					
CH4	16.90	17.09	17.52	17.58	18.13
C2 HC'S	2.48	2.50	2.55	2.66	2.69
C3H8	3.24	3.42	3.41	3.57	3.45
C3H6=	1.99	2.03	1.95	1.99	1.99
C4H10	2.51	2.69	2.57	2.68	2.64
C4H8=	3.20	3.40	3.34	3.50	3.26
C5H12	3.03	3.09	3.08	3.24	3.17
C5H10=	3.77	3.90	3.74	3.92	4.06
C6H14	3.07	3.24	3.13	3.13	3.36
C6H12= & CYCLO'S	3.15	3.19	3.06	3.17	2.32
C7+ IN GAS	10.47	10.52	10.98	10.91	11.06
LIQ HC'S	46.20	44.95	44.66	43.66	43.87
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 18 (continued)

SUB-GROUPING					
C1 -C4	30.31	31.11	31.34	31.99	32.16
C5 -420 F	45.20	44.91	44.84	40.51	40.20
420-700 F	19.86	19.58	19.45	21.89	21.99
700-END PT	4.62	4.40	4.37	5.61	5.64
C5+-END PT	69.69	68.89	68.66	68.01	67.84
ISO/NORMAL MOLE RATIO					
C4	0.0561	0.0550	0.0516	0.0531	0.0488
C5	0.0718	0.0746	0.0678	0.0685	0.0686
C6	0.1624	0.1637	0.1646	0.1590	0.1783
C4=	0.0710	0.0714	0.0729	0.0736	0.0750
PARAFFIN/OLEFIN RATIO					
C3	1.5539	1.6100	1.6678	1.7091	1.6514
C4	0.7569	0.7654	0.7437	0.7400	0.7804
C5	0.7815	0.7715	0.8018	0.8029	0.7603
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))	0.8252		0.8217	0.8367	0.8391
RATIO CH4/(1-A)**2	5.5305		5.5090	6.5956	6.9994
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY BL		OIL/SLD		OIL/SLD
DENSITY	0.7580		0.7510		0.7517
N, REFRACTIVE INDEX	1.4263		1.4264		1.4264
SIMULT'D DISTILATN					
10 WT % @ DEG F	285		290		301
16	304		305		331
50	439		442		489
84	644		638		679
90	700		697		721
RANGE(16-84 %)	340		333		348
WT % @ 420 F	47.00	46.66	46.66	37.00	37.00
WT % @ 700 F	90.00	90.21	90.21	87.14	87.14

Table 19

RESULT OF SYNGAS OPERATION

RUN NO. 11723-12
CATALYST HiCoThU103+U101+CuZnAl2O3 250CC 120.GM (167 AFTER RUN +47 G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 302 GHSV

RUN & SAMPLE NO.	11723-12-21	723-12-22	723-12-23	723-12-24	723-12-25
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	244.0	261.5	268.0	286.3	292.7
PRESSURE,PSIG	299	299	297	297	297
TEMP. C	265	265	265	266	265
FEED CC/MIN	1260	1260	1260	1260	1260
HOURS FEEDING	6.50	24.00	6.50	24.75	6.42
EFFLNT GAS LITER	281.75	1045.35	283.50	1079.25	276.35
GM AQUEOUS LAYER	47.67	176.02	47.99	182.74	47.90
GM OIL	17.35	64.07	18.36	69.90	17.29
MATERIAL BALANCE					
GM ATOM CARBON %	94.37	94.20	96.47	97.73	95.29
GM ATOM HYDROGEN %	100.58	101.22	102.35	103.00	100.78
GM ATOM OXYGEN %	97.87	97.66	98.82	99.40	98.56
RATIO CHX/(H2O+CO2)	0.8886	0.8894	0.9259	0.9473	0.8975
RATIO X IN CHX	2.4187	2.4200	2.4163	2.4663	2.4215
USAGE H2/CO PRODT	2.0075	2.0155	1.9634	1.9741	2.0022
FEED H2/CO FRM EFFLNT	1.0658	1.0746	1.0610	1.0539	1.0576
RESIDUAL H2/CO RATIO	0.6069	0.6177	0.5997	0.5798	0.5869
RATIO CO2/(H2O+CO2)	0.0967	0.0940	0.1015	0.1002	0.0965
K SHIFT IN EFFLNT	0.0649	0.0641	0.0677	0.0646	0.0627
SPECIFIC ACTIVITY SA	0.7224	0.7050	0.7717	0.7770	0.7776
CONVERSION					
ON CO %	32.77	32.68	33.83	34.00	33.26
ON H2 %	61.72	61.30	62.60	63.69	62.96
ON CO+H2 %	47.70	47.51	48.64	49.23	48.52
PRDT SELECTIVITY,WT %					
CH4	18.38	18.51	18.32	18.24	18.65
C2 HC'S	2.79	2.69	2.74	2.72	2.72
C3H8	3.52	3.49	3.47	3.71	3.40
C3H6=	1.95	1.87	1.85	2.20	1.96
C4H10	2.78	2.69	2.67	2.77	2.66
C4H8=	3.36	3.23	3.28	3.59	3.32
C5H12	3.22	3.15	3.06	2.98	3.04
C5H10=	3.86	3.81	3.84	3.75	4.02
C6H14	3.29	3.28	3.31	3.23	3.28
C6H12= & CYCLO'S	3.28	3.03	3.10	3.02	3.24
C7+ IN GAS	10.98	11.59	11.63	12.09	11.83
LIQ HC'S	42.58	42.66	42.74	41.68	41.88
TOTAL	100.00	100.00	100.00	100.00	100.00

Table 19 (continued)

SUB-GROUPING					
C1 -C4	32.78	32.48	32.32	33.24	32.71
C5 -420 F	44.65	44.91	44.17	43.83	44.26
420-700 F	18.44	18.47	19.28	18.84	18.96
700-END PT	4.13	4.13	4.23	4.08	4.08
C5+-END PT	67.22	67.52	67.68	66.76	67.29
ISO/NORMAL MOLE RATIO					
C4	0.0510	0.0480	0.0529	0.1078	0.0509
C5	0.0684	0.0654	0.0710	0.0690	0.0662
C6	0.1623	0.1512	0.1607	0.1607	0.1400
C4=	0.0743	0.0737	0.0768	0.0883	0.0726
PARAFFIN/OLEFIN RATIO					
C3	1.7252	1.7834	1.7922	1.6112	1.6577
C4	0.7986	0.8025	0.7864	0.7437	0.7736
C5	0.8112	0.8041	0.7731	0.7717	0.7350
SCHULZ-FLORY DISTRBTN					
ALPHA (EXP(SLOPE))		0.8182		0.8176	
RATIO CH4/(1-A)**2		5.6040		5.4842	
LIQ HC COLLECTION					
PHYS. APPEARANCE		OIL/SLD		OIL/SLD	
DENSITY		0.7577		0.7587	
N, REFRACTIVE INDEX		1.4264		1.4265	
SIMULT'D DISTILATN					
10 WT % @ DEG F		294		288	
16		306		303	
50		439		444	
84		633		639	
90		696		699	
RANGE(16-84 %)		327		336	
WT % @ 420 F	47.00	47.00	45.00	45.00	45.00
WT % @ 700 F	90.31	90.31	90.10	90.20	90.27

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Table 20

RESULT OF SYNGAS OPERATION

RUN NO. 11723-12
CATALYST HiCoThU103+U101+CuZnAl2O3 250CC 120 GM (167 AFTER RUN +47 G)
FEED H2:CO:ARGON OF 50:50:0 @ 1260 CC/MN OR 402 GHSV

RUN & SAMPLE NO.	11723-12-26
FEED H2:CO:AR	50:50: 0
HRS ON STREAM	309.3
PRESSURE,PSIG	294
TEMP. C	266
FEED CC/MIN	1260
HOURS FEEDING	23.08
EFFLNT GAS LITER	999.65
GM AQUEOUS LAYER	172.33
GM OIL	62.19
MATERIAL BALANCE	
GM ATOM CARBON %	96.27
GM ATOM HYDROGEN %	101.92
GM ATOM OXYGEN %	98.77
RATIO CHX/(H2O+CO2)	0.9215
RATIO X IN CHX	2.4221
USAGE H2/CO PRODT	1.9850
FEED H2/CO FRM EFFLNT	1.0587
RESIDUAL H2/CO RATIO	0.5879
RATIO CO2/(H2O+CO2)	0.0961
K SHIFT IN EFFLNT	0.0625
SPECIFIC ACTIVITY SA	0.7632
CONVERSION	
ON CO %	33.70
ON H2 %	63.19
ON CO+H2 %	48.87
PRDT SELECTIVITY,WT %	
CH4	18.41
C2 HC'S	2.79
C3H8	3.66
C3H6=	2.11
C4H10	3.06
C4H8=	3.66
C5H12	3.35
C5H10=	4.22
C6H14	3.31
C6H12= & CYCLO'S	3.34
C7+ IN GAS	11.29
LIQ HC'S	40.79
TOTAL	100.00

Table 20 (continued)

SUB-GROUPING	
C1 -C4	33.69
C5 -420 F	43.87
420-700 F	18.47
700-END PT	3.97
C5+-END PT	66.31
ISO/NORMAL MOLE RATIO	
C4	0.0933
C5	0.0776
C6	0.1761
C4=	0.0928
PARAFFIN/OLEFIN RATIO	
C3	1.6573
C4	0.8074
C5	0.7709
SCHULZ-FLORY DISTRBTN	
ALPHA (EXP(SLOPE))	0.8152
RATIO CH4/(1-A)**2	5.3902
LIQ HC COLLECTION	
PHYS. APPEARANCE	OIL/SLD
DENSITY	0.7590
N, REFRACTIVE INDEX	1.4266
SIMULT'D DISTILATN	
10 WT % @ DEG F	290
16	303
50	445
84	637
90	697
RANGE(16-84 %)	334
WT % @ 420 F	45.00
WT % @ 700 F	90.27

IX. Run 8 (11677-20) with Catalyst 8 (Cu/Zn/LZ-105-6)

This run continues the search for an effective water gas shift catalyst which will not deactivate in the presence of a Fischer-Tropsch component; as in Run 5, this test is for water gas shift activity alone. LZ-105-6 is a Union Carbide acidic zeolite of the ZSM-5 type which is highly resistant to coking and is used for the conversion of small olefins.

The LZ-105-6 was loaded in one step with copper and zinc in a ratio of 1:2, bonded with SiO_2, and formed as an extrudate.

The test procedure was the same as in Run 5. As Table 21 shows, this catalyst had no significant water gas shift activity, even in the absence of a Fischer-Tropsch catalyst.

Table 21

RESULT OF WATER GAS SHIFT REACTION

RUN NO. 11677-20
CATALYST CU/ZN-PF-LZ-105-6 #11864-044 80 CC 39.4 GM
FEED H2O:CO:H2 OF 3:3:1 @ 14CC/HR & 400 CC(CO+H2)/MN,TOTAL 525 GHSV

	11677-20-03	677-20-04	677-20-05
FEED H2O:CO:H2	31:30:10	31:30:10	31:30:10
HRS ON STREAM	18.0	25.5	41.5
PRESSURE,PSIG	300	300	296
TEMP. C	257	258	258
FEED (CO+H2)CC/MN	400	400	400
FEED WATER CC/HR	14	14	14
HOURS FEEDING	18.0	7.5	23.50
EFFLNT GAS LITER	444.95	184.75	390.00
GM AQUEOUS LAYER	209.19	97.82	306.51
MATERIAL BALANCE			
GM MOLE H2O %	86.95	96.67	95.34
GM MOLE CO %	100.92	100.97	68.08
GM MOLE H2 %	95.96	95.62	65.21
K SHIFT IN EFFLNT	0.0048	0.0027	0.0009
CONVERSION			
ON H2O %	1.43	0.827	0.289
ON CO %	1.29	0.829	0.424
ON H2O+CO %	1.35	0.828	0.344

X. Run 9 (11677-21) with Catalyst 9 (Cu/Zn/LZ-105-6)

This catalyst was prepared in the same way as Catalyst 8 except that the LZ-105-6 was zinc-ion exchanged before being loaded with copper.

As Table 22 shows, it had no water gas shift activity. The inadequacy of this catalyst, and of Catalyst 8, may be due to the inability of the copper and zinc to form a suitable oxide environment in the acidic, highly siliceous environment of LZ-105-6.

Table 22

RESULT OF WATER GAS SHIFT REACTION

RUN NO. 11677-21
CATALYST Cu-PF-Zn/LZ-105-6 #11864-02C 80 CC 39.7 GM
FEED H2O:CO:H2 OF 3:3:1 @ 14CC/HR & 400 CC(CO+H2)/MN,TOTAL 525 GHSV

	11677-21-01	677-21-02	677-21-03
FEED H2O:CO:H2	31:30:10	31:30:10	31:30:10
HRS ON STREAM	23.75	30.75	47.75
PRESSURE,PSIG	295	296	297
TEMP. C	261	261	262
FEED (CO+H2)CC/MN	400	400	400
FEED WATER CC/HR	15.7	15.7	15.7
HOURS FEEDING	23.75	7.0	24.00
EFFLNT GAS LITER	590.00	173.05	595.00
GM AQUEOUS LAYER	362.61	108.92	373.43
MATERIAL BALANCE			
GM MOLE H2O %	99.84	101.69	101.67
GM MOLE CO %	102.60	102.01	102.46
GM MOLE H2 %	96.27	96.05	95.95
K SHIFT IN EFFLNT	0.0004	0.0004	0.0003
CONVERSION			
ON H2O %	0.121	0.111	0.096
ON CO %	0.138	0.130	0.112
ON H2O+CO %	0.129	0.120	0.103

XI. Run 10 (11677-18) with Catalyst 10 (Co/Th/UCC-103+Cu/Zn/LZ-105-6)

This catalyst is a mixture of separate particles of Fischer-Tropsch catalyst (Co/Th/UCC-103) and water gas shift catalyst (Cu/Zn/LZ-105-6), the Fischer-Tropsch component being similar to Catalyst 7 (Run 10225-16) of the Eleventh Quarterly Report. The lack of water gas shift activity of the latter catalyst prompted the separate test of the water gas shift component two runs later (Run 11677-20), which is reported as Run 8 of this Report.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C_4's are plotted against time on stream in Figs. 115-118. Simulated distillations of the C_5^+ product are plotted in Figs. 119-121. Carbon number product distributions are plotted in Figs. 122-126. Chromatograms from simulated distillations are reproduced in Figs. 127-131. Detailed material balances appear in Tables 23-24.

The water gas shift activity was no better than that of the Fischer-Tropsch catalyst when it was tested separately. Less than 10 percent of the oxygen was rejected as CO_2. Interestingly, both the conversion and the specific activity improved steadily with time on stream. If the first two samples are excluded, the rate of improvement was 0.08 percent per hour; the levels were still low at the end of the run, but if the same rate of im-

provement were to continue another few hundred hours the activity would be substantial.

There is no apparent explanation for the difference between the first two samples and all the others. Like the conversion, the selectivity improved with time. The production of methane decreased one percent every 48 hours, and at the end of the test, although a little high at more than 16 percent, it was still decreasing. The production of C_5^+ increased one percent every 43 hours, and the production of C_2-C_4 decreased gradually throughout the test. The liquid product became heavier with time, the gasoline remaining fairly constant while the diesel and heavies were increasing. The C_4's were less olefinic than usual and the pentane was not very highly isomerized.

The performance of this catalyst was disappointing for its unremarkable activity and especially for its lack of the water gas shift activity which was hoped from it. It is nonetheless of some interest for its pattern of steady improvement with time, at least for the duration of the run.

Fig. 115

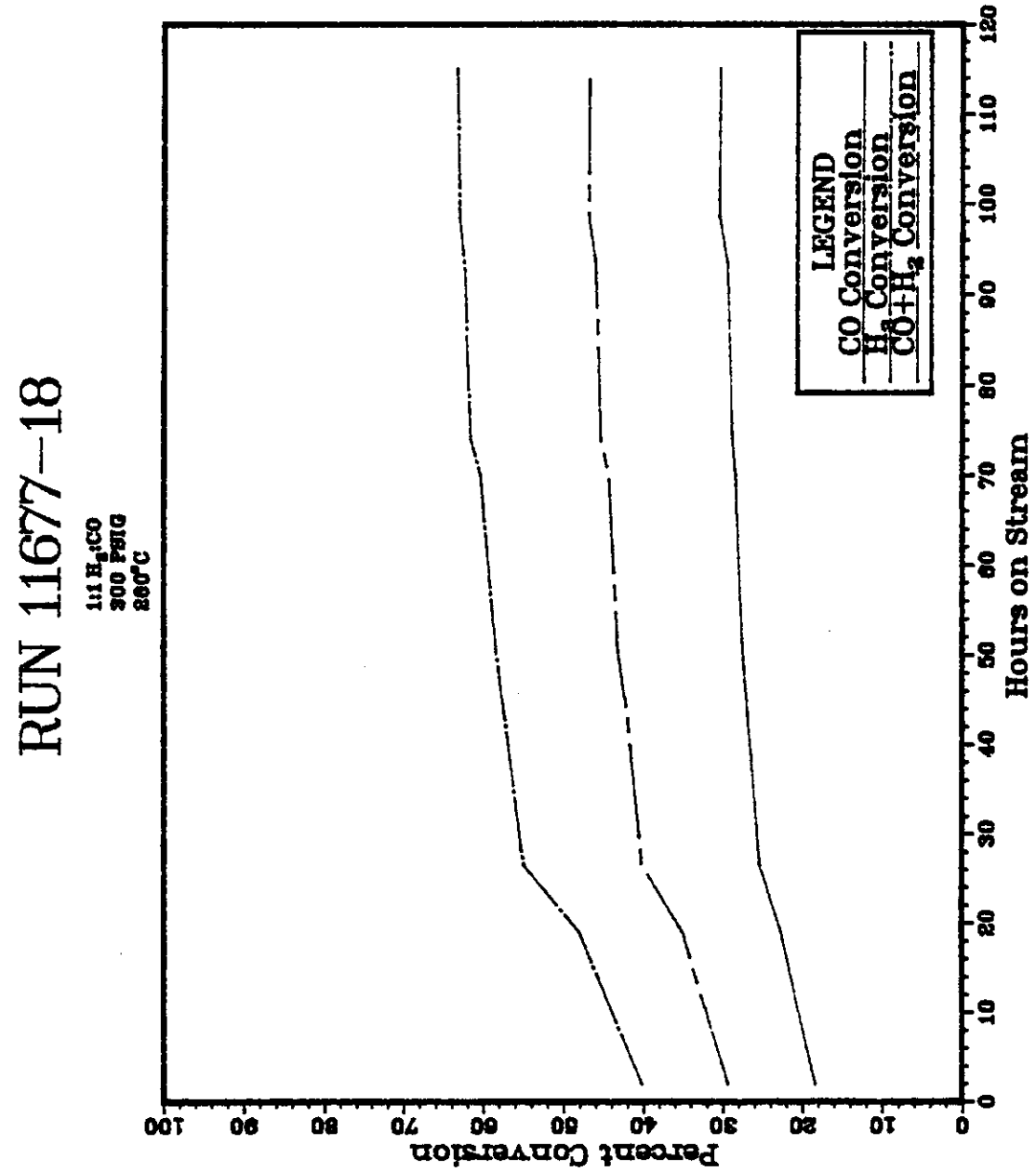

RUN 11677-18
1:1 H2:CO
200 PSIG
260°C
LEGEND
CO Conversion
H2 Conversion
CO+H2 Conversion
Percent Conversion
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
110
120

Fig. 116

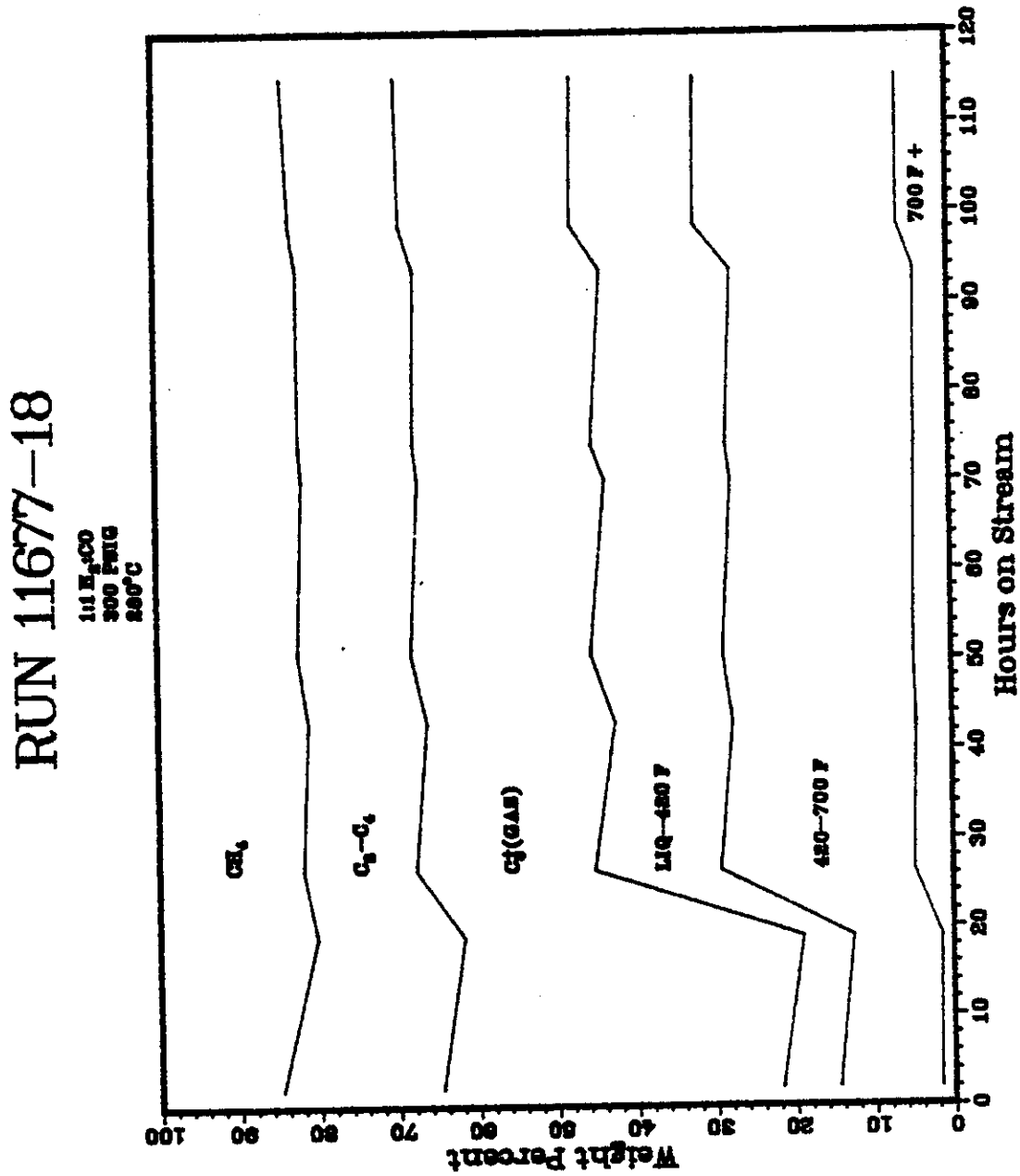

RUN 11677–18
Weight Percent
Hours on Stream
700 F +
420–700 F
110–420 F
C5–C6
CH4

Fig. 117

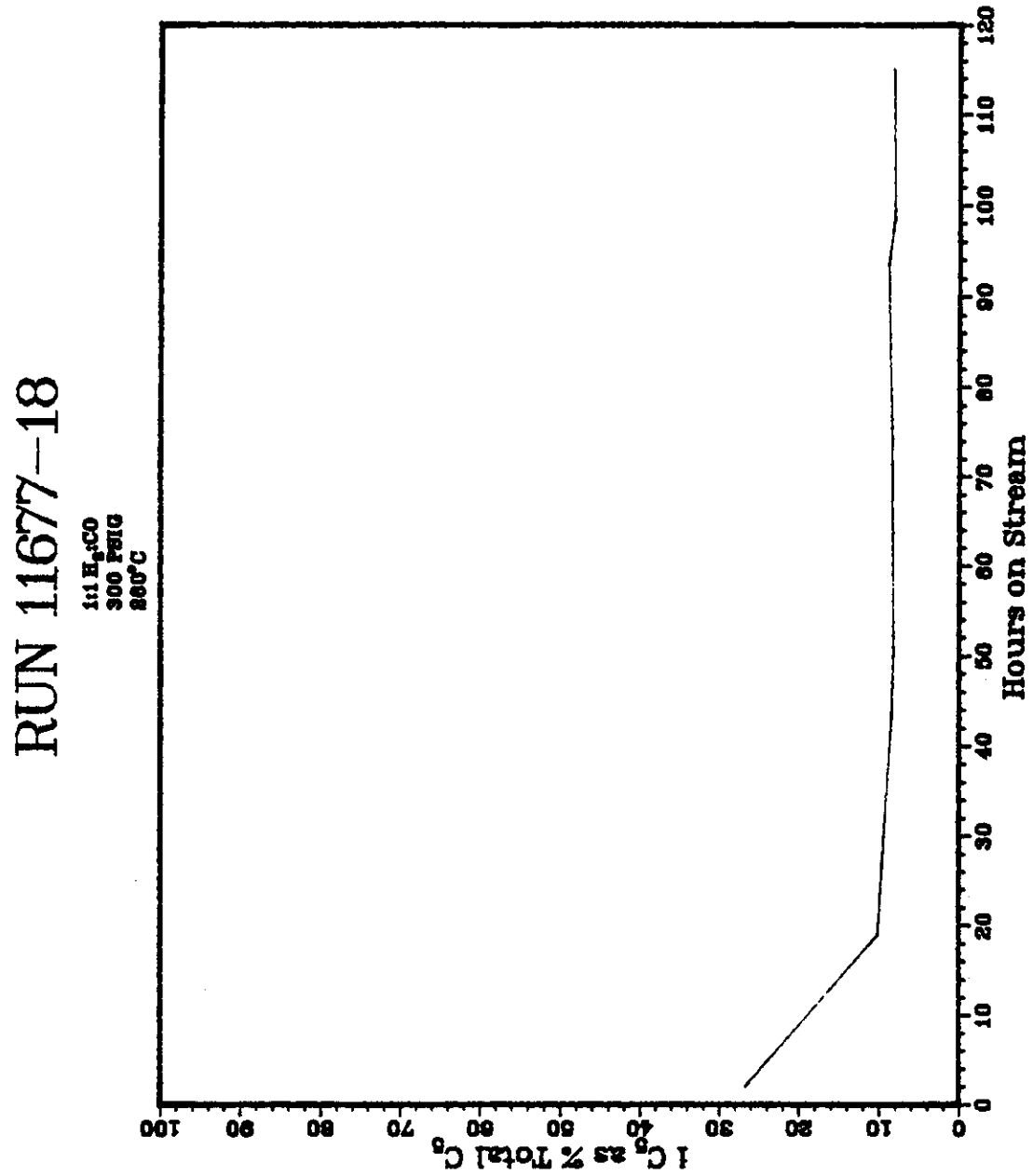

RUN 11677-18
1:1 H2:CO
300 Psig
260°C
i C5 as % Total C5
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
110
120

Fig. 118

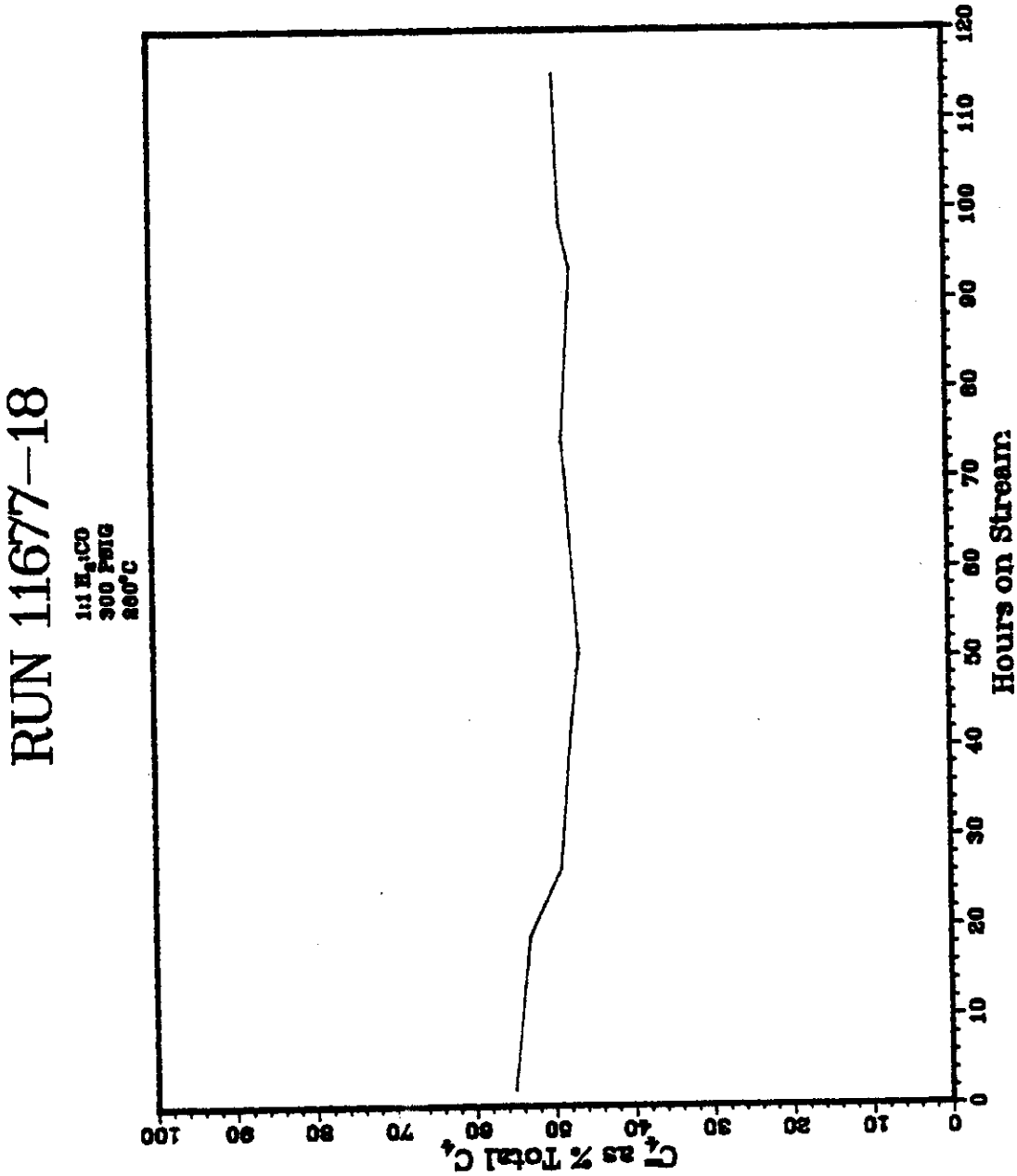

RUN 11677-18
1:1 H2:CO
300 PSIG
260°C
C4 as % Total C4
Hours on Stream
0
10
20
30
40
50
60
70
80
90
100
110
120

Fig. 119

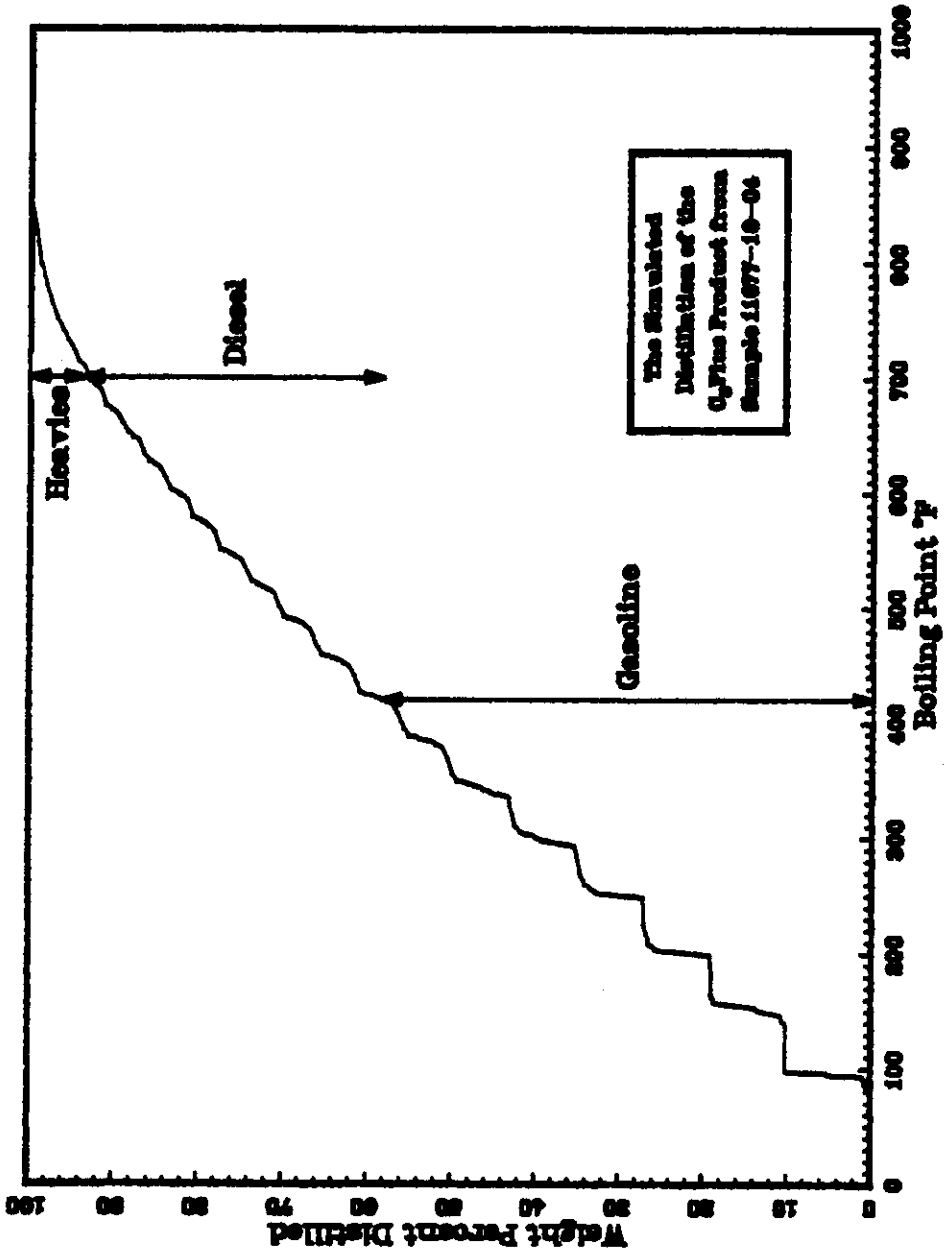
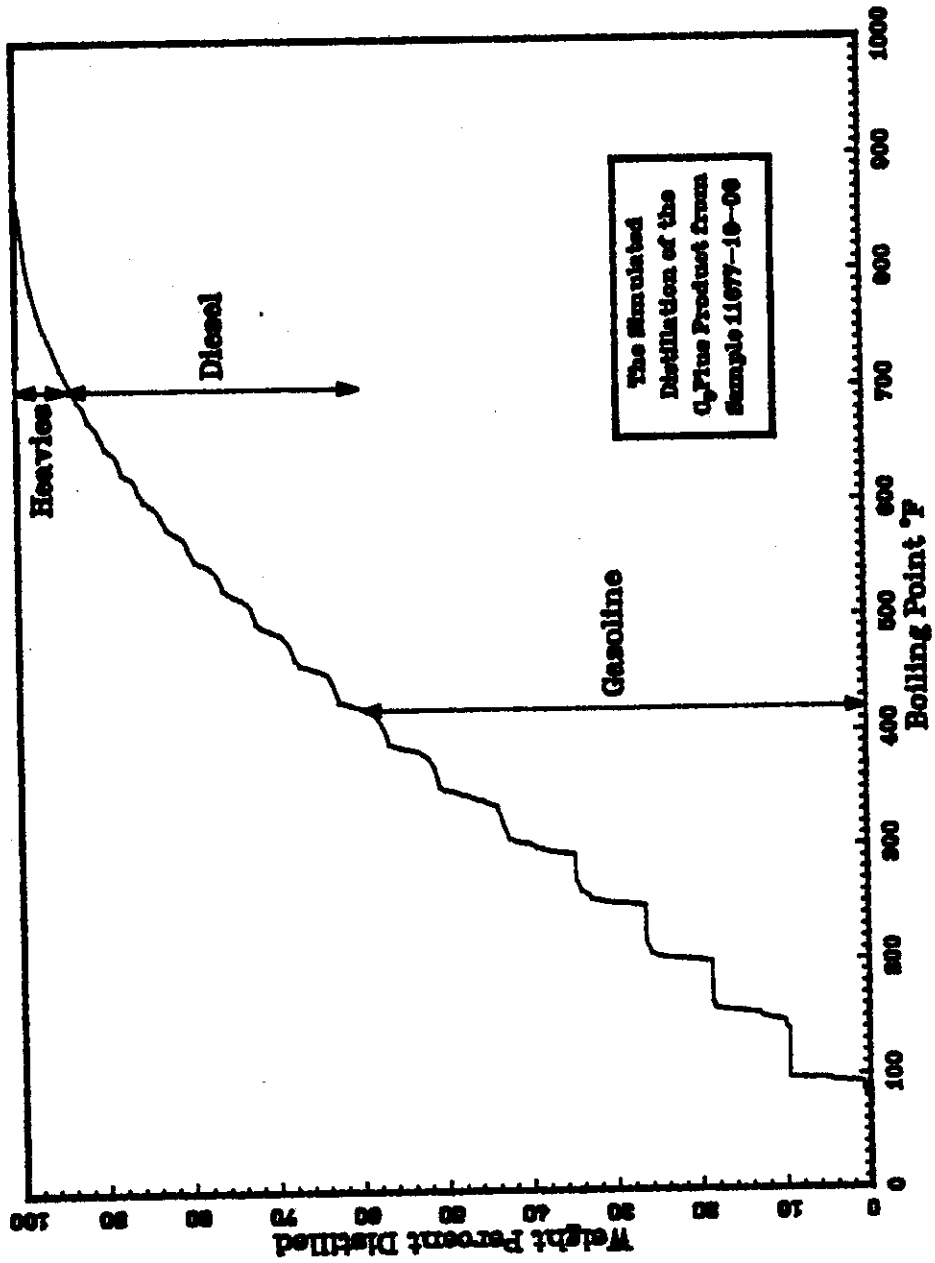

Heavies
Diesel
Gasoline
Weight Percent Distilled
Boiling Point °F
0
100
200
300
400
500
600
700
800
900
1000

Fig. 120


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