

OVER TEMP NOT READ:

99T

ST: 3.1255 2.20

1-1-1 TEMP=32°C SETP=32°C LIMIT=405°C

1-1-1 TEMP=32°C SETP=32°C LIMIT=405°C

1-1-1 TEMP=32°C SETP=32°C LIMIT=405°C

1-1-1 TEMP=32°C SETP=32°C LIMIT=405°C

1-1-1 TEMP=40°C SETP=40°C LIMIT=405°C

1-1-1 TEMP=40°C

1-1-1 3.1255 2.20

Fig. B20

- B25 -

09T

RT: 11123 3.10

1: IVE- TEP=20°C SETP=22°C LIMIT=405°C

2: IVE- TEP=80°C SETP=82°C LIMIT=405°C

3: IVE- TEP=200°C SETP=200°C LIMIT=405°C

4: IVE- TEP=320°C SETP=320°C LIMIT=405°C

5: IVE- TEP=400°C SETP=400°C LIMIT=405°C

IVE STOP RUN

RT: 1112351-21-23

Fig. B22

Table B1

RESULT OF SYNGAS OPERATION

RUN NO.	12561-01				
CATALYST	CO/X9/X10-103 80 CC 37.1 G AFTER USE:58.0 (+20.9 G)				
FEED	H2:CO OF 50:50 @ 400 CC/MIN OR 300 GHSV (CAT#12524-13)				
RUN & SAMPLE NO.	12561-01-01	561-01-02	561-01-03	561-01-04	561-01-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	21.2	47.5	68.5	92.0	117.0
PRESSURE, PSIG	300	300	300	300	300
TEMP. C	241	240	239	239	244
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	21.20	26.25	21.00	25.00	25.00
EFFLNT GAS LITER	218.50	352.10	263.00	361.50	345.00
GM AQUEOUS LAYER	58.98	57.13	40.22	50.44	51.37
GM OIL	12.40	28.61	30.05	35.57	35.16
MATERIAL BALANCE					
GM ATOM CARBON %	67.39	89.93	88.70	98.49	95.49
GM ATOM HYDROGEN %	82.70	96.74	95.35	104.47	103.37
GM ATOM OXYGEN %	86.27	93.24	84.81	95.29	92.26
RATIO CHX/(H2O+CO2)	0.4694	0.8846	1.1549	1.1200	1.1191
RATIO X IN CHX	2.4083	2.3304	2.2822	2.3002	2.3162
USAGE H2/CO PRODT	2.7353	2.0479	1.8505	1.8796	1.8759
FEED H2/CO FRM EFFLNT	1.2273	1.0757	1.0750	1.0608	1.0825
RESIDUAL H2/CO RATIO	0.6183	0.6496	0.6668	0.6747	0.6783
RATIO CO2/(H2O+CO2)	0.0753	0.0719	0.0634	0.0636	0.0684
K SHIFT IN EFFLNT	0.0503	0.0503	0.0451	0.0458	0.0498
SPECIFIC ACTIVITY SA	2.2072	2.4230	2.9389	2.5928	2.0883
CONVERSION					
ON CO %	28.76	30.47	34.48	32.04	33.75
ON H2 %	64.11	58.01	59.36	56.78	58.49
ON CO+H2 %	48.24	44.74	47.37	44.77	46.61
PRDT SELECTIVITY, WT %					
CH4	15.30	10.76	8.36	9.31	10.06
C2 HC'S	1.09	1.69	1.21	1.25	1.43
C3H8	2.95	2.07	1.56	1.66	1.85
C3H6=	3.14	2.76	2.13	2.19	2.22
C4H10	2.89	2.17	1.62	1.79	1.94
C4H8=	3.80	3.11	2.46	2.56	2.58
C5H12	3.11	2.44	1.83	2.06	2.27
C5H10=	2.77	2.38	1.80	1.86	1.88
C6H14	4.44	3.43	2.67	2.89	2.98
C6H12= & CYCLO'S	1.60	1.39	1.09	1.18	1.10
C7+ IN GAS	9.80	7.14	5.42	5.90	6.31
LIQ HC'S	49.11	60.65	69.84	67.33	65.37
TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	29.17	22.56	17.35	18.77	20.08
C5 -420 F	42.35	36.25		29.18	
420-700 F	26.72	28.99		26.33	
700-END PT	1.77	12.19		25.72	

Table B1 (continued)
 FILE: 1256101A TSS1Q2 A1

CS+-END PT	70.83	77.44	82.65	81.23	79.92
ISO/NORMAL MOLE RATIO					
C4	0.0220	0.0251	0.0191	0.0210	0.0263
C5	0.0736	0.0614	0.0605	0.0612	0.0613
C6	0.2986	0.2558	0.2661	0.2311	0.2523
C4=	0.0644	0.0591	0.0629	0.0546	0.0641
PARAFFIN/OLEFIN RATIO					
C3	0.8949	0.7153	0.7017	0.7240	0.7951
C4	0.7332	0.6753	0.6377	0.6739	0.7258
C5	1.0930	0.9973	0.9855	1.0777	1.1699
SCHULZ-FLORY DISTRIBUTION					
ALPHA (EXP(SLOPE))	0.8062	0.8440	0.7894	0.8777	0.7885
RATIO CH4/(1-A)**2	4.0755	4.4197	1.8901	6.2267	2.2476
ALPHA FRM CORRELATION	0.8353	0.8330		0.8312	
ALPHA (EXPTL/CORR)	0.9652	1.0132		1.0560	
WYCH4 FRM CORRELATION	14.7625	15.2636		15.5909	
WYCH4 (EXPTL/CORR)	1.0365	0.7049		0.5973	
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLD OIL	CLD OIL	OIL WAX	OIL WAX	OIL WAX
DENSITY					
N, REFRACTIVE INDEX					
SIMULT'D DISTILLATE					
10 WT % @ DEG F	297	302		337	
16	336	342		378	
50	452	513		613	
84	592	744		908	
90	632	858		989	
RANGE(16-84 %)	256	402		530	
WT % @ 420 F	42.00	32.10		22.70	
WT % @ 700 F	96.40	79.90		61.80	

Table B2

RESULT OF SYNGAS OPERATION

RUN NO. 12561-01
 CATALYST CO/X9/X10-U103 80 CC 37.1 G AFTER USE:58.0 G (+20.9 G)
 FEED H2:CO OF 50:50 @ 400 CC/MIN OR 300 GHSV (CAT#12524-13)

RUN & SAMPLE NO.	12561-01-06	561-01-07	561-01-08
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	140.0	164.0	235.0
PRESSURE, PSIG	300	300	300
TEMP. C	240	239	239
FEED CC/MIN	400	400	400
HOURS FEEDING	23.00	24.00	71.00
EFFLNT GAS LITER	343.00	340.00	1051.00
GM AQUEOUS LAYER	44.04	44.45	136.71
GM OIL	27.30	28.86	84.12
MATERIAL BALANCE			
GM ATOM CARBON %	95.72	91.98	94.64
GM ATOM HYDROGEN %	102.47	99.15	102.15
GM ATOM OXYGEN %	94.62	90.08	93.78
RATIO CHX/(H2O+CO2)	1.0436	1.0784	1.0341
RATIO X IN CHX	2.3190	2.3165	2.3203
USAGE H2/CO PRODT	1.9712	1.9486	1.9956
FEED H2/CO FRM EFFLNT	1.0705	1.0779	1.0794
RESIDUAL H2/CO RATIO	0.7061	0.7085	0.7112
RATIO CO2/(H2O+CO2)	0.0515	0.0501	0.0454
% SHIFT IN EFFLNT	0.0383	0.0374	0.0338
SPECIFIC ACTIVITY SA	2.0098	2.2054	2.0915
CONVERSION			
ON CO %	28.81	29.79	28.66
ON H2 %	53.05	53.85	53.00
ON CO+H2 %	41.34	42.27	41.30
PRDT SELECTIVITY, WT %			
CH4	10.29	10.09	10.57
C2 HC'S	1.29	1.61	1.58
C3H8	1.94	1.84	2.02
C3H6=	1.80	2.33	2.50
C4H10	2.07	1.96	2.16
C4H8=	2.83	2.67	2.86
CSH12	2.41	2.31	2.54
CSH10=	2.05	1.90	2.06
CSH14	3.09	2.93	0.91
CSH12+ & CYCLO'S	0.91	0.87	1.13
C7+ IN GAS	7.58	6.65	7.33
LIQ HC'S	63.75	64.83	64.34
TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	20.21	20.50	21.68
C5 -420 F	32.68	32.24	32.12
420-700 F	26.84	27.68	27.54
700-END PT	20.27	19.58	18.66

FILE: 1256101B TSS1Q2 Table B2 (continued)
AI

C5+-END PT	79.79	79.50	78.32
ISO/NORMAL MOLE RATIO			
C4	0.0000	0.0000	0.0000
C5	0.0537	0.0545	0.0639
C6	0.2202	0.2247	2.4468
C4=	0.0598	0.0576	0.0611
PARAFFIN/OLEFIN RATIO			
C3	1.0298	0.7555	0.7716
C4	0.7043	0.7098	0.7286
C5	1.1421	1.1809	1.1982
SCHULZ-FLORY DISTRBTN			
ALPHA (EXP(SLOPE))	0.8745	0.8719	0.8727
RATIO CH4/(1-A)**2	6.5303	6.1475	6.5224
ALPHA FRM CORRELATION	0.8289	0.8288	0.8286
ALPHA (EXPTL/CORR)	1.0550	1.0520	1.0532
WYCH4 FRM CORRELATION	16.5232	16.3299	16.3863
WYCH4 (EXPTL/CORR)	0.6225	0.6176	0.6449
LIQ HC COLLECTION			
PHYS. APPEARANCE	OIL WAX	OIL WAX	OIL WAX
DENSITY			
N, REFRACTIVE INDEX			
SIMULT'D DISTILATN			
10 WT % @ DEG F	335	335	328
16	373	372	359
50	568	563	548
84	826	826	821
90	887	897	898
RANGE(16-84 %)	453	454	462
WT % @ 420 F	26.10	27.10	28.20
WT % @ 700 F	68.20	69.80	71.00

III. Run 45 (12570-02) with Catalyst 45 (Co/X₁₁/TC-123)

The purpose of Runs 45 and 46 was to evaluate two newly developed Molecular Sieves in comparison with TC-103, the most effective catalyst support developed to date; this run tested TC-123. Except for a slightly different pretreatment, the catalyst was formulated by the same method as the promising Catalyst 32 (Fourth Quarterly Report, Co/X₁₁/TC-103). The theoretical content of Co and X₁₁, respectively, was 8.2 and 1.6 percent.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. B23-26. Simulated distillations of the C₅⁺ product are plotted in Figs. B27-49. Carbon number product distributions are plotted in Figs. B50-72. Chromatograms from simulated distillations are reproduced in Figs. B73-95. Detailed material balances appear in Tables B3-13.

The test was run for 1568 hours, more than twice the duration of the longest previous run in either contract. The test conditions were varied in eight stages, A through H.

Both conversion and stability were excellent during Stage A (259 hours on stream at 240C, 1:1 H₂:CO, 300 psig). The syngas conversion averaged about 47 percent, the methane production 3.6 percent, and the C₅⁺ production about 90 percent (the first data point was excluded in each calculation). Corresponding values

with the TC-103 containing Catalyst 32 were about 42 percent, 5.5 percent, and about 85 percent.

Similar improvements were obtained in the quality of the light gas fraction, C₂-C₄. The ratio of paraffins to olefins of the C₄'s was 0.36:1 and the olefin content was 73 percent, as against 0.50:1 and 67 percent respectively with the TC-103 catalyst. From these results, the performance of TC-123 improves substantially upon that of TC-103.

A low methane production permits the use of higher H₂:CO ratio feed to help achieve higher catalytic activity. The feed was accordingly adjusted, in Stages B and C, to 1.5:1 and 1.75:1 H₂:CO respectively. The results, as compared with the TC-103 catalyst, were as follows (GHSV=300, 300 psig):

	Catalyst 45 TC-123 Stage B	Catalyst 45 TC-123 Stage C	Catalyst 32 TC-103
Temp, deg C	240	240	260
H ₂ :CO	1.5:1	1.75:1	1:1
Conversion, pct	57.7	62.2	58.0
Wt pct CH ₄	6.1	11.5	7.6
C ₅ ⁺ , pct	86.3	80.1	82.1

In Stage B, therefore, the conversion of this catalyst was about the same at 240C as that of Catalyst 32 at 260C, but with substantially better selectivity. In Stage C, raising the feed H₂:CO ratio nearly doubled the methane production but raised the conversion only 4.5 percentage points. Again the stability, in both stages, was excellent.

Stage D tested the effect of raising the pressure from 300

to 500 psig while maintaining all other conditions as in Stage C. As usual with the typical Fischer-Tropsch catalyst, the result was an initial increase in activity (from 62 to about 70 percent), and a heavier product (methane reduced from about 12 to about 7 percent, and C_5^+ increased from about 80 to about 85 percent). The stability suffered, however, with conversion falling during the 331 hours in this stage at a rate of about one percentage point every 83 hours. Such poor stability has usually been accompanied by progressively degraded selectivity, but this time the methane production remained constant at the relatively low level of about 7 percent.

At two points during this stage, following Samples 25 and 31, the catalyst was briefly exposed to a pure hydrogen feed in an attempt to boost its activity. Only a slight improvement resulted, but if this is done at regular intervals throughout the run it may possibly serve to maintain the conversion at a more or less constant level.

In Stage E, when the $H_2:CO$ feed ratio was raised again to 1.85:1, there was a slight increase in conversion, a two percent increase in methane production, and little or no effect on stability.

Two other variations tested were an increase in space velocity from 400 to 833 cc per minute in Stage F, and a reduction in temperature from 240 to 220C in Stage G.

In Stage H, which concluded the run, the conditions of Stage C were restored with the purpose of assessing the overall effect

of the various process conditions which had been tested. By this time the catalyst had substantially deteriorated both in activity (conversion about 45 percent as against a high of 61 percent) and in selectivity (methane production about 14 percent as against a low of 11 percent).

This is an important catalyst for its demonstration of the superior properties of the Molecular Sieve TC-123 in yielding high conversion, low methane, and high olefin content, as compared with a similar formulation containing TC-103. The low methane production, in turn, makes it possible to enhance the catalyst's activity still further by operating it in a more hydrogen-rich environment than usual.

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Test conditions at each stage (Figs. 23-26)

<u>Stage</u>	<u>H₂:CO</u>	<u>psig</u>	<u>deg C</u>	<u>cc/min</u>
A	1:1	300	240	400
B	1.5:1	"	"	"
C	1.75:1	"	"	"
D	"	500	"	"
E	1.85:1	"	"	"
F	1.75:1	"	"	833
G	"	"	220	400
H	"	300	240	"

RUN 12570-02

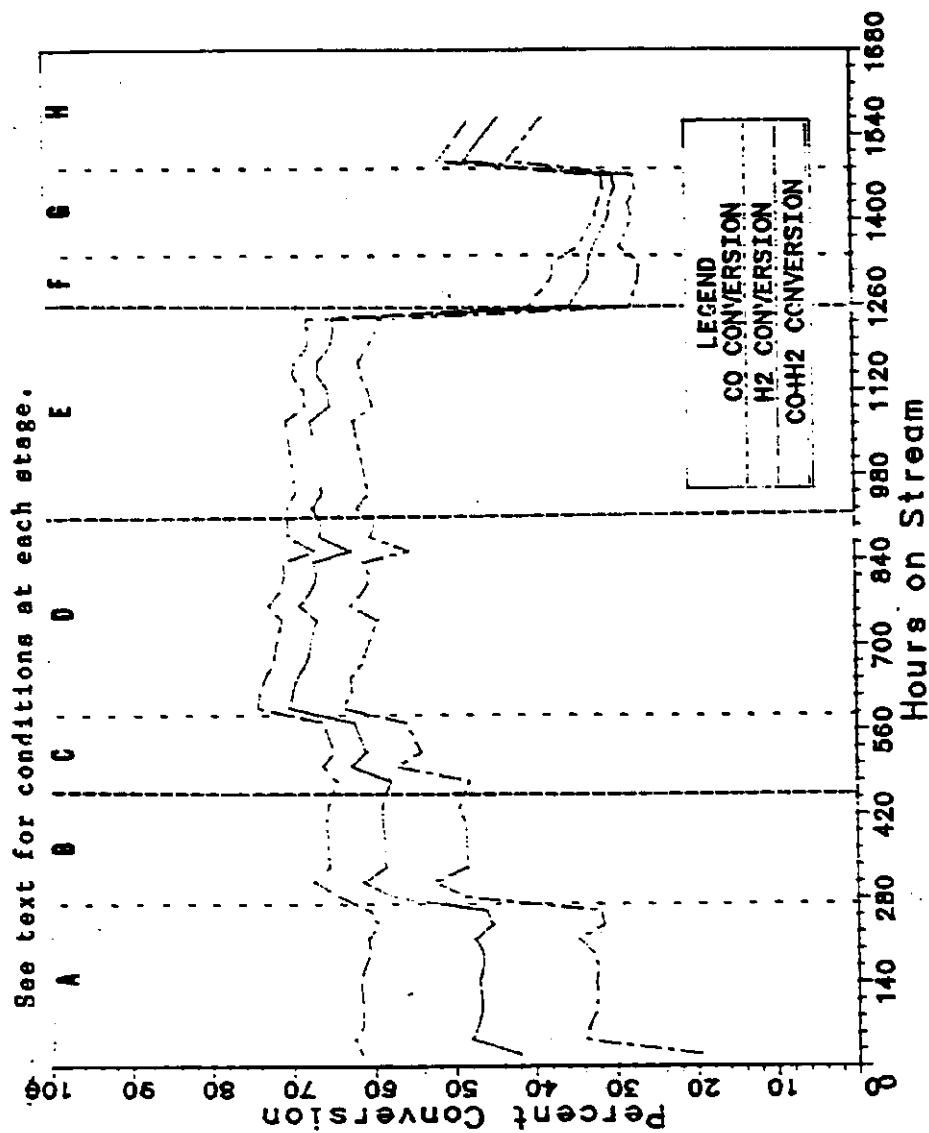


Fig. B23

RUN 12570-02

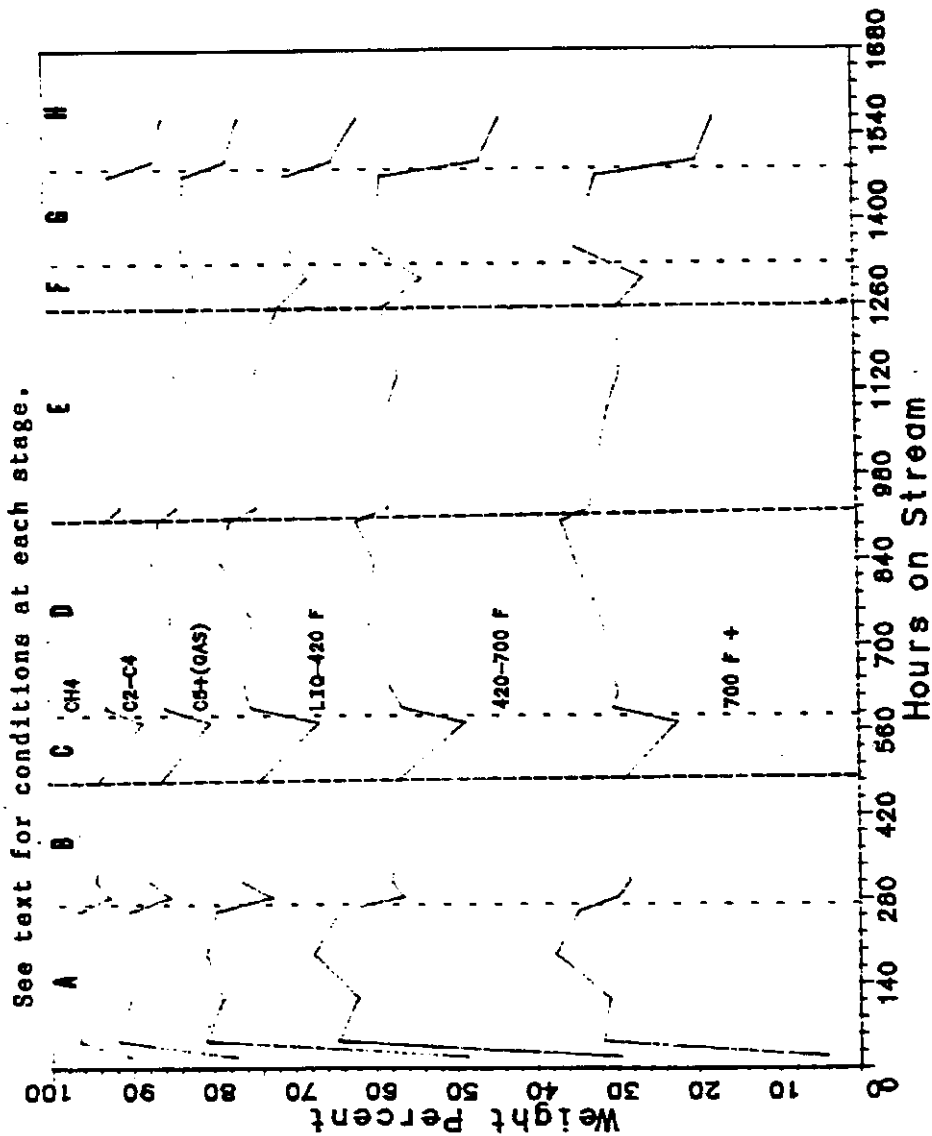


Fig. B24

RUN 12570-02

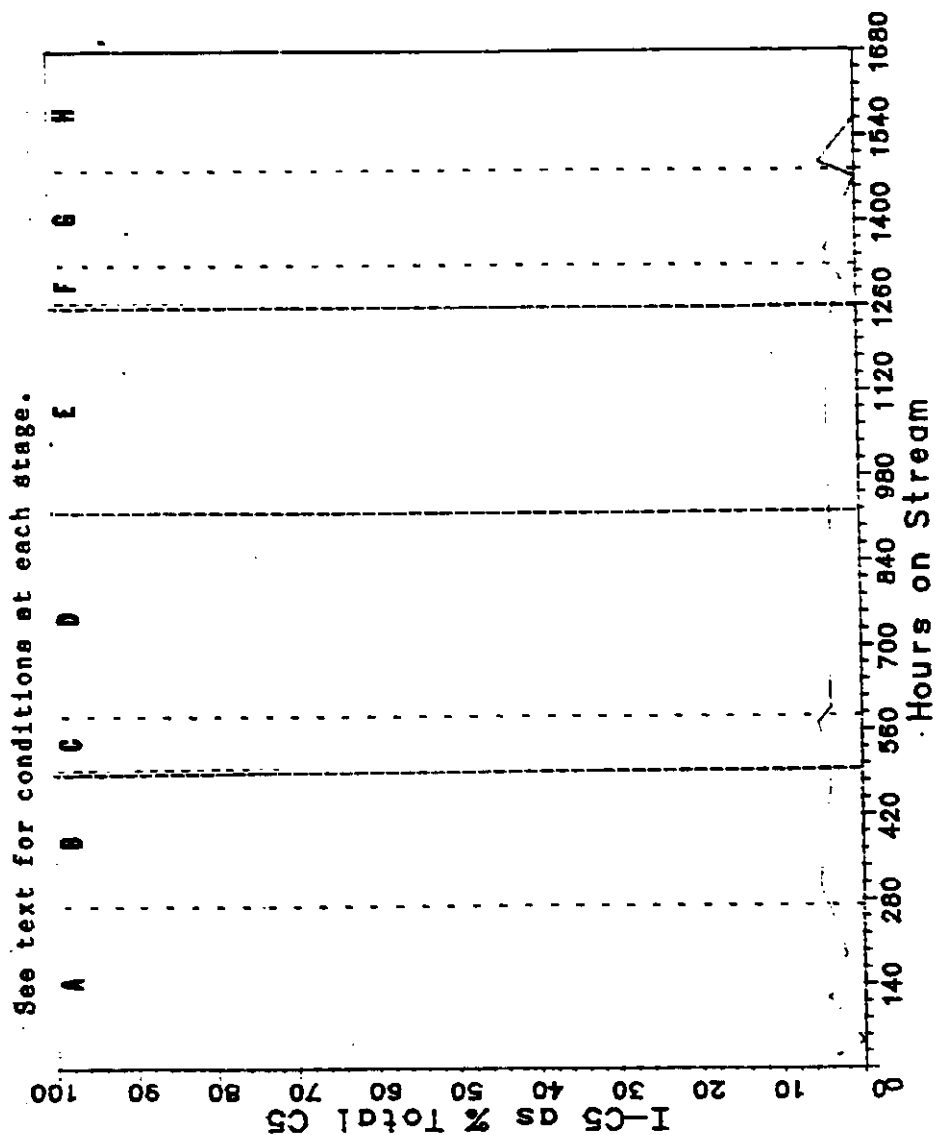


Fig. B25

RUN 12570-02

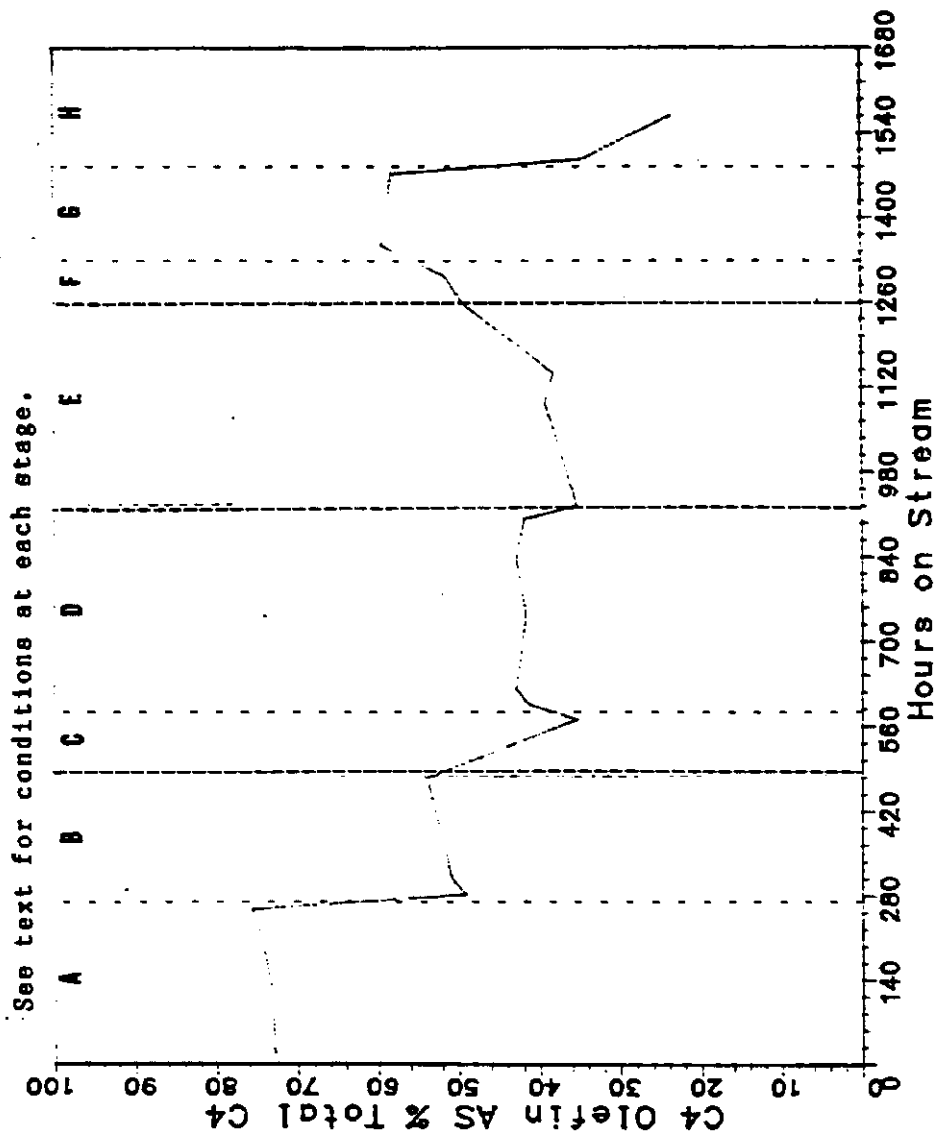


Fig. B26

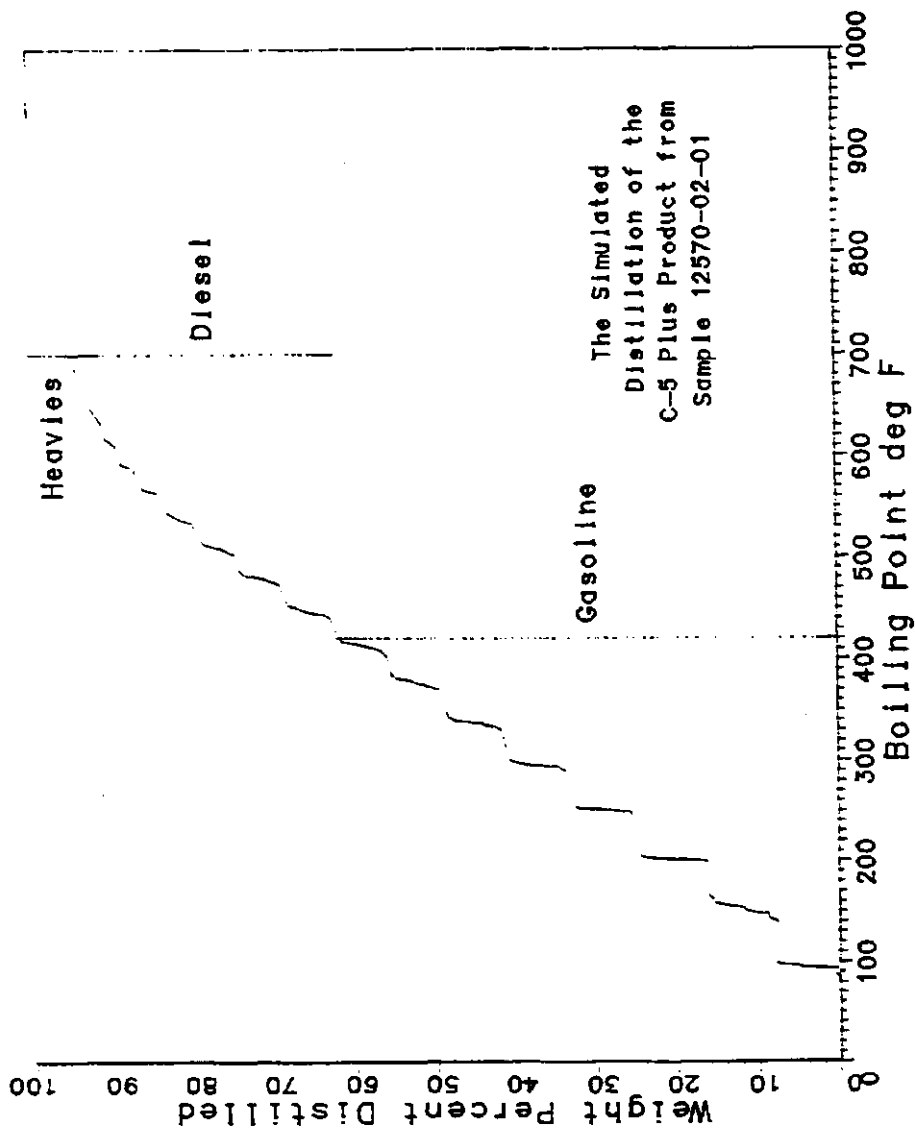


Fig. B27

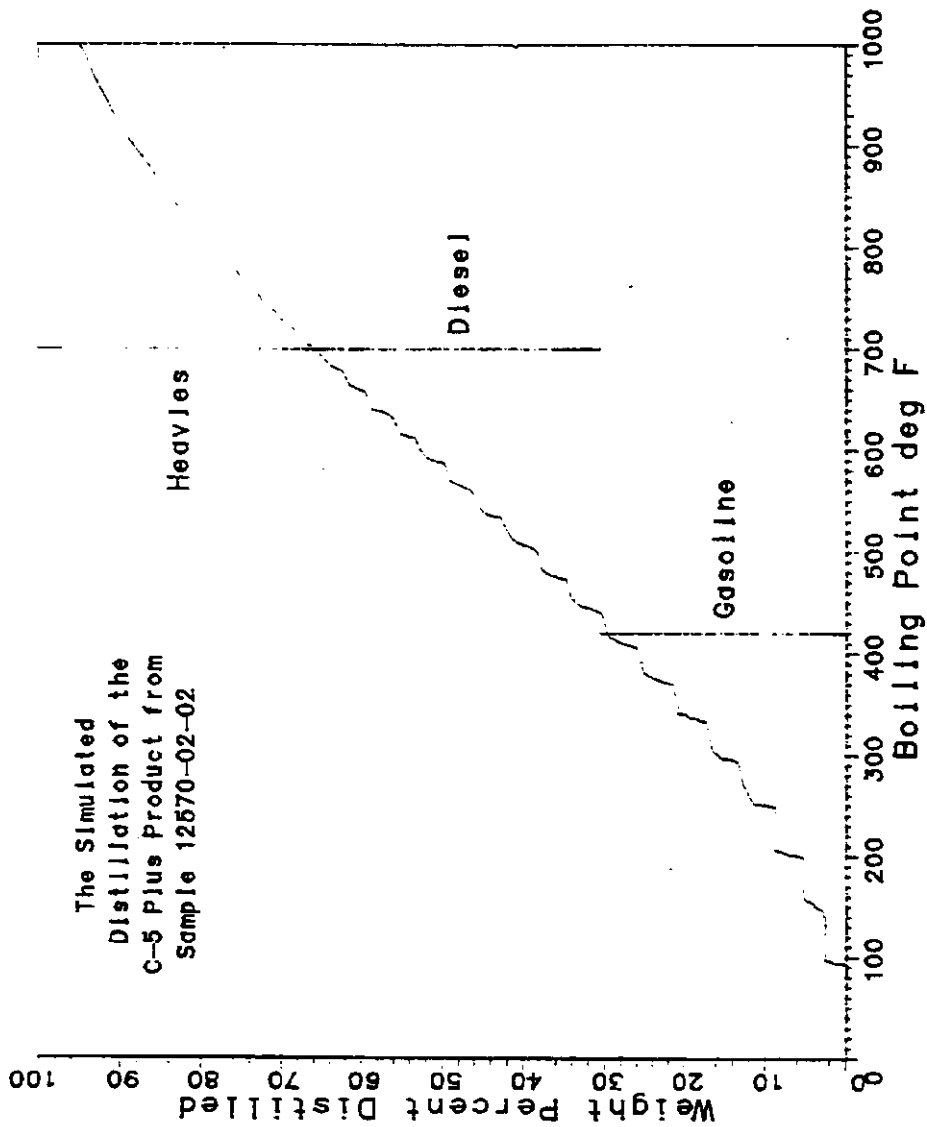


Fig. B28

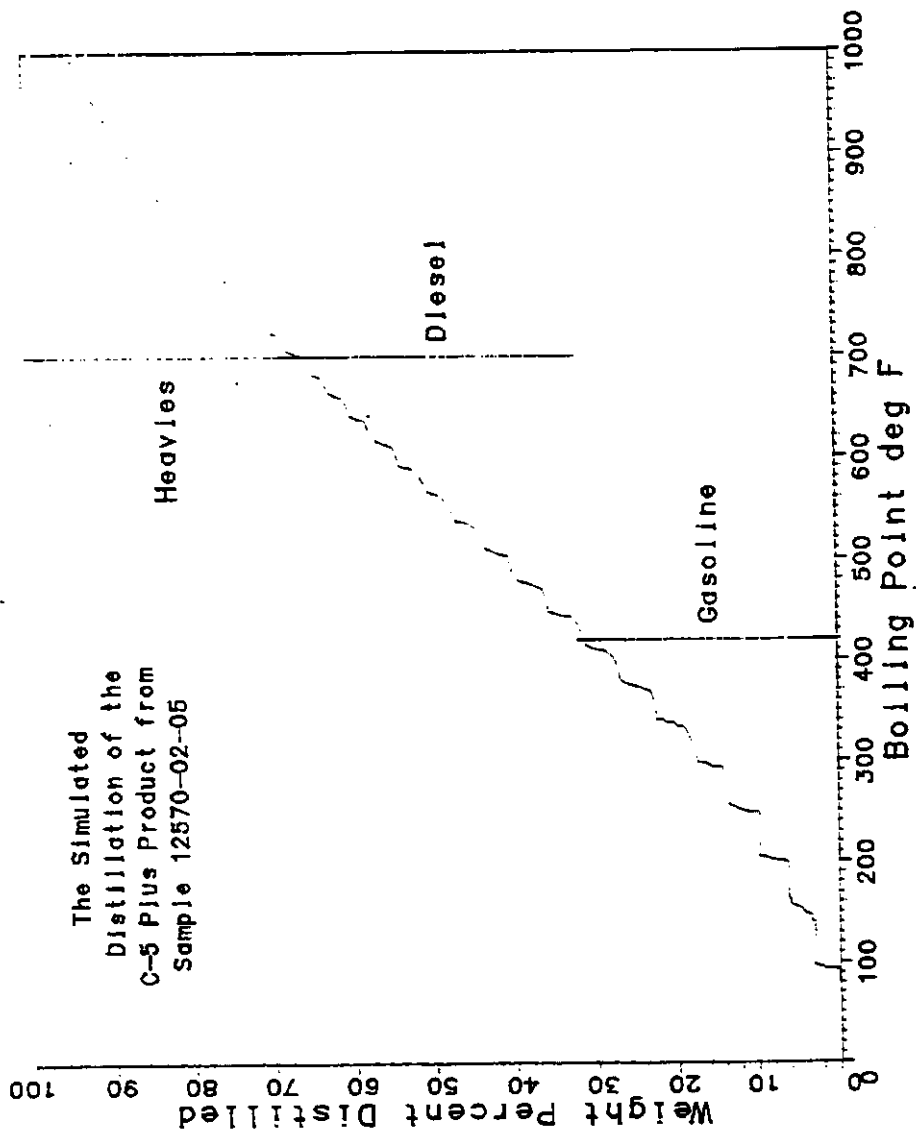


Fig. B29

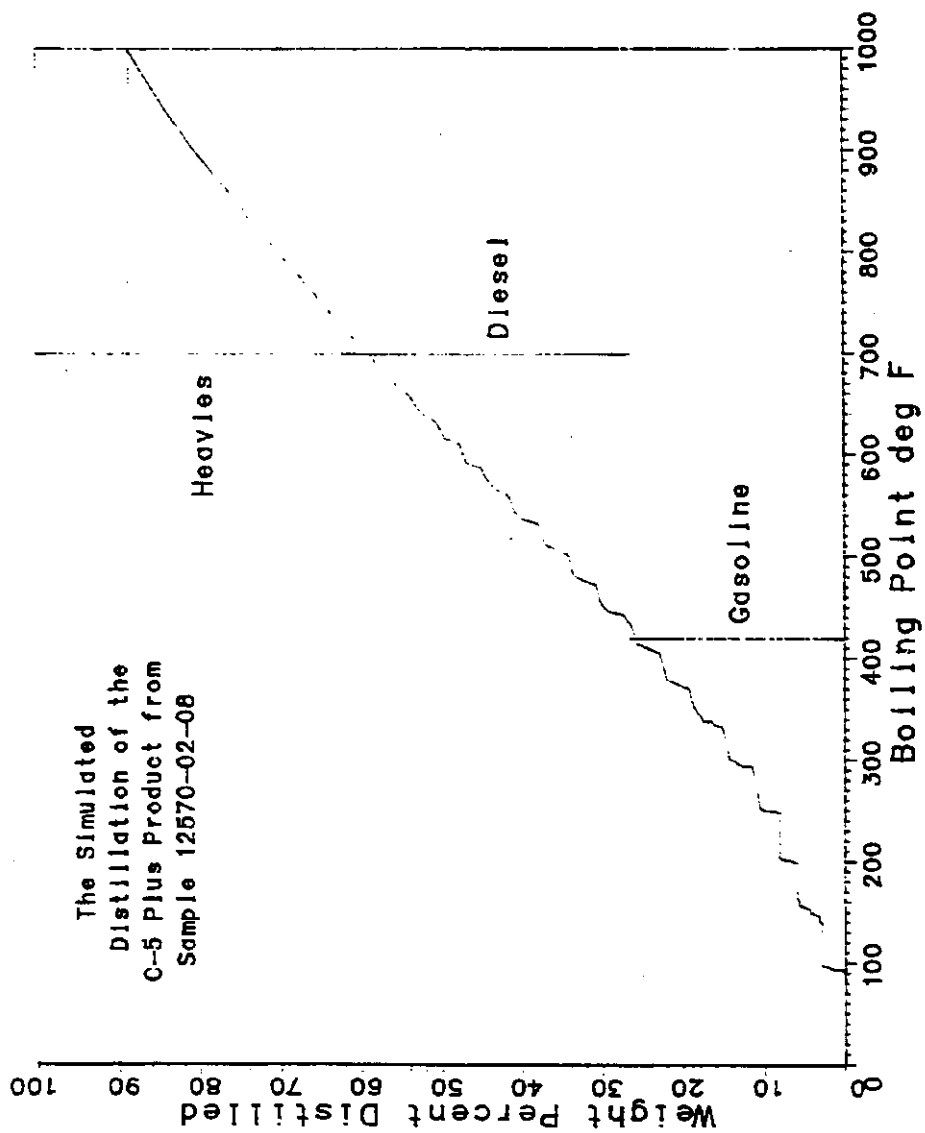


Fig. B30

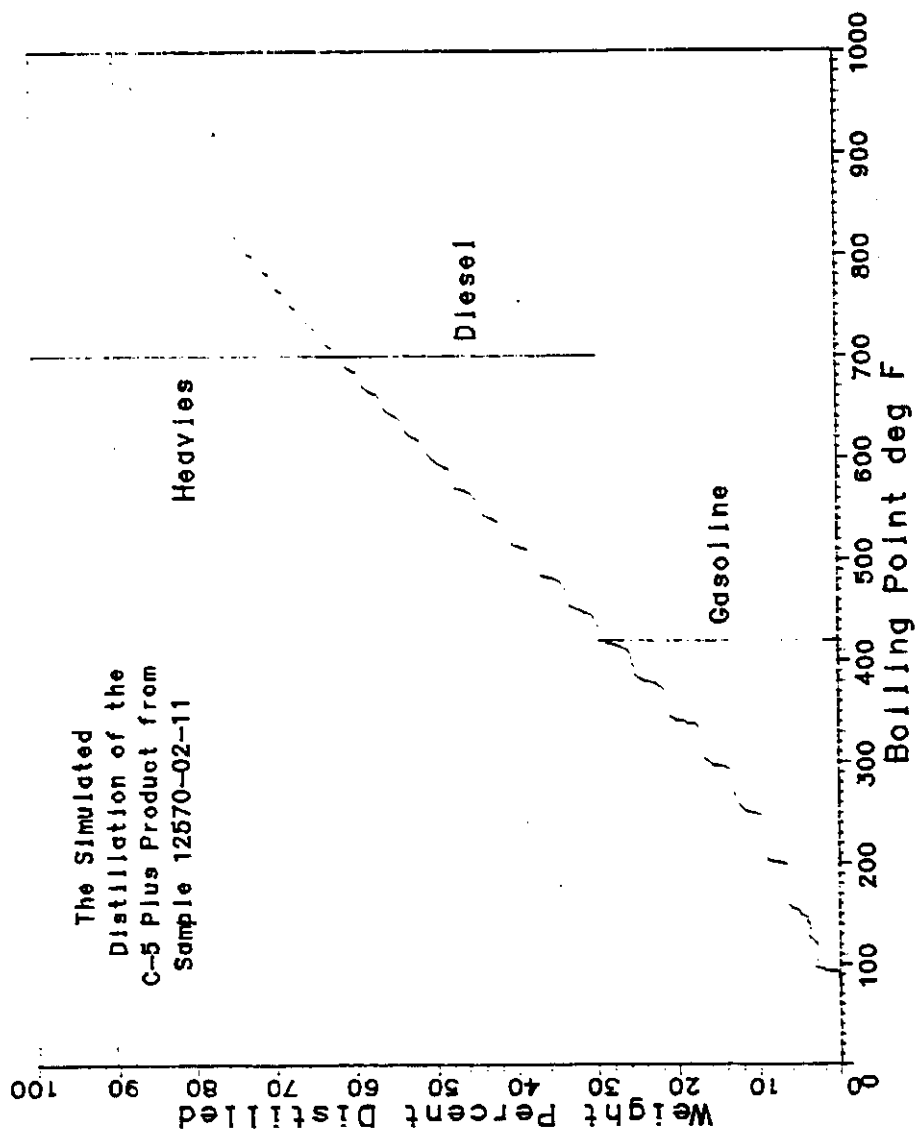


Fig. B31

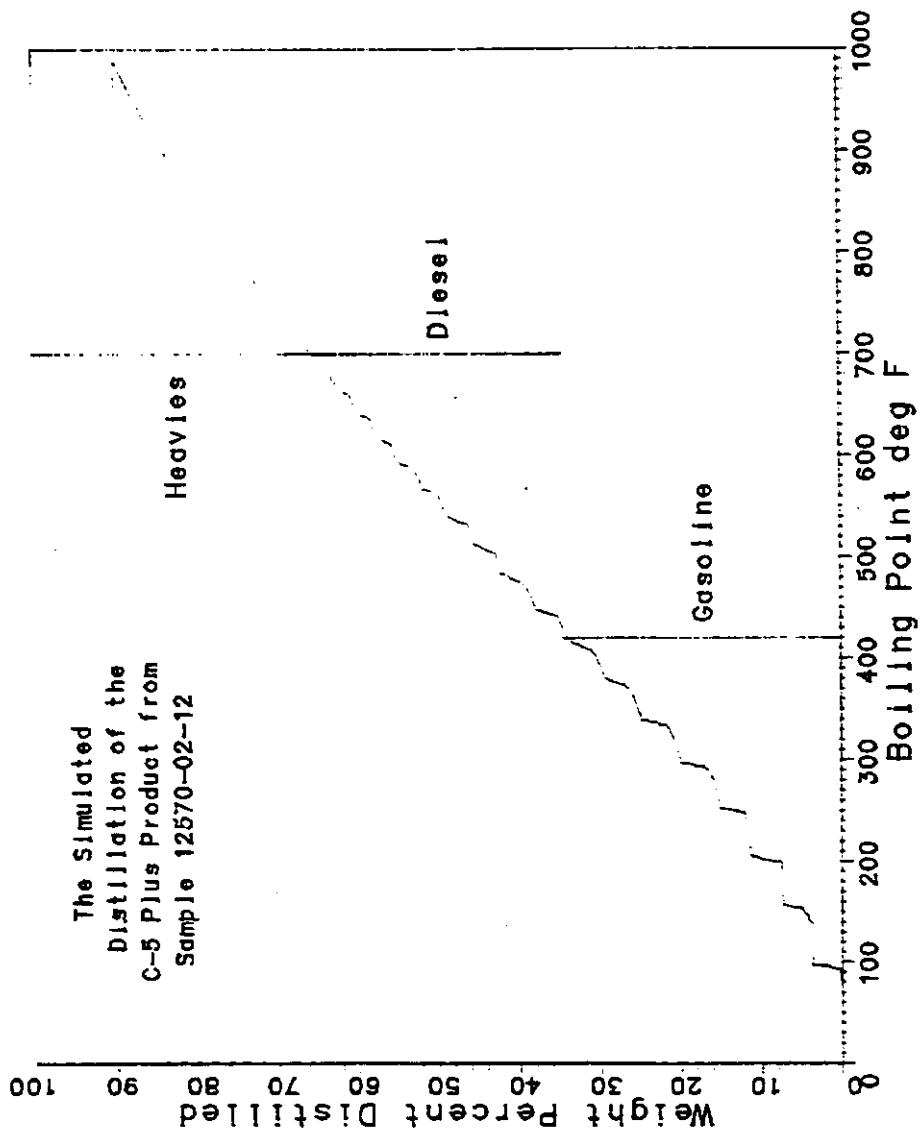


Fig. B32

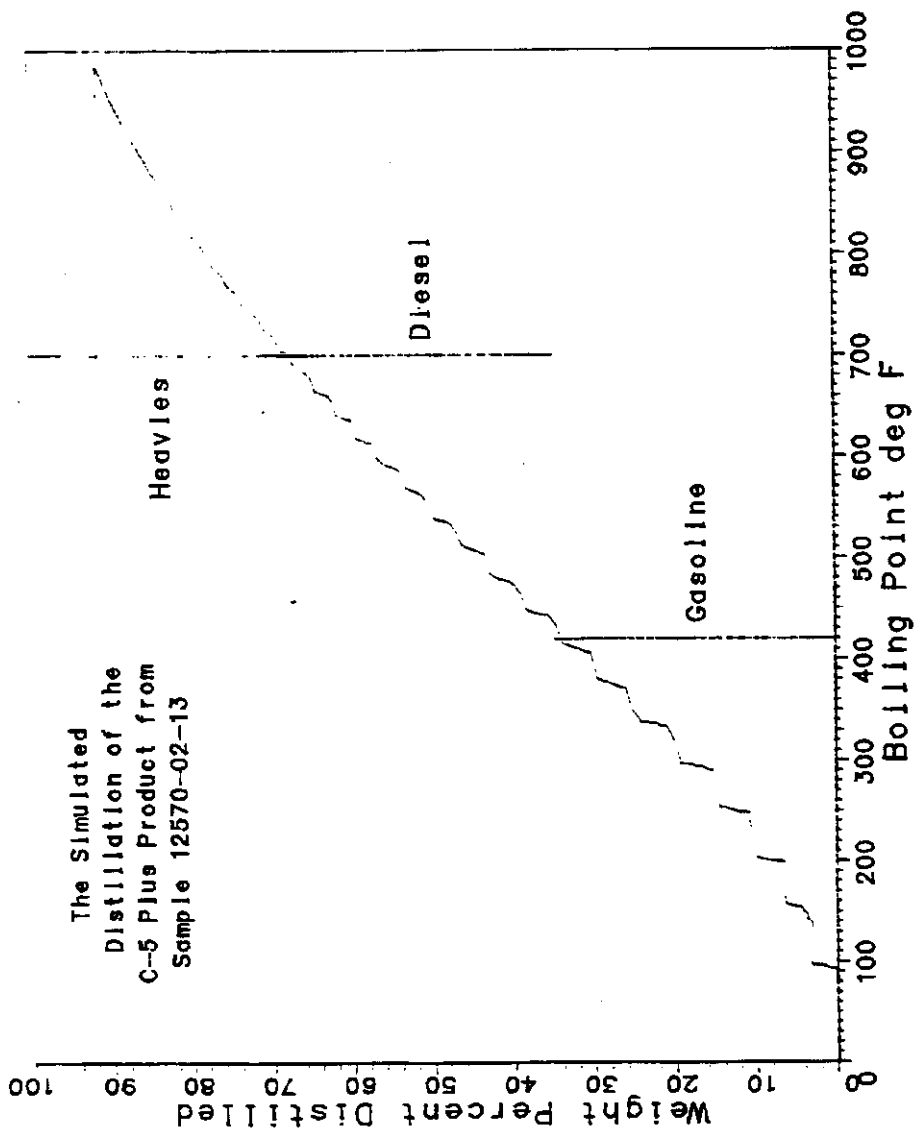


Fig. B33

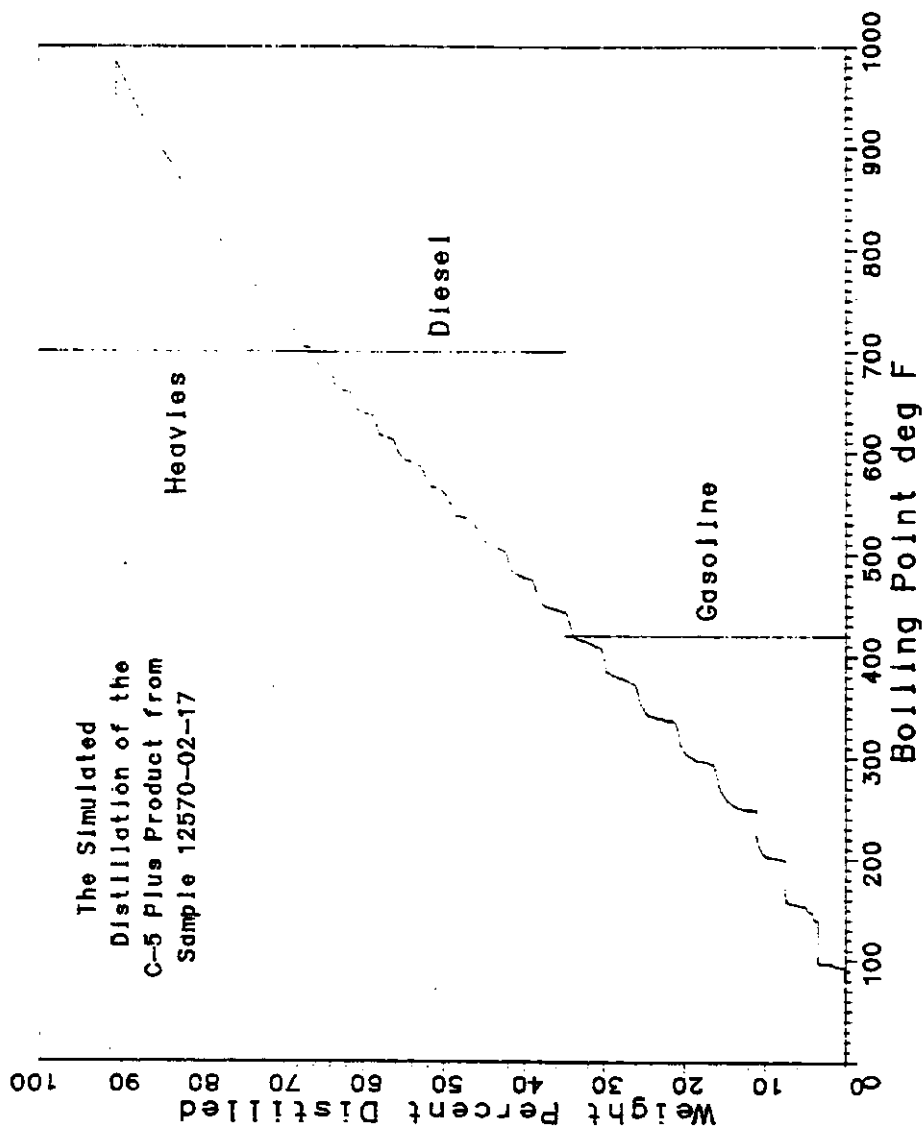


Fig. B34

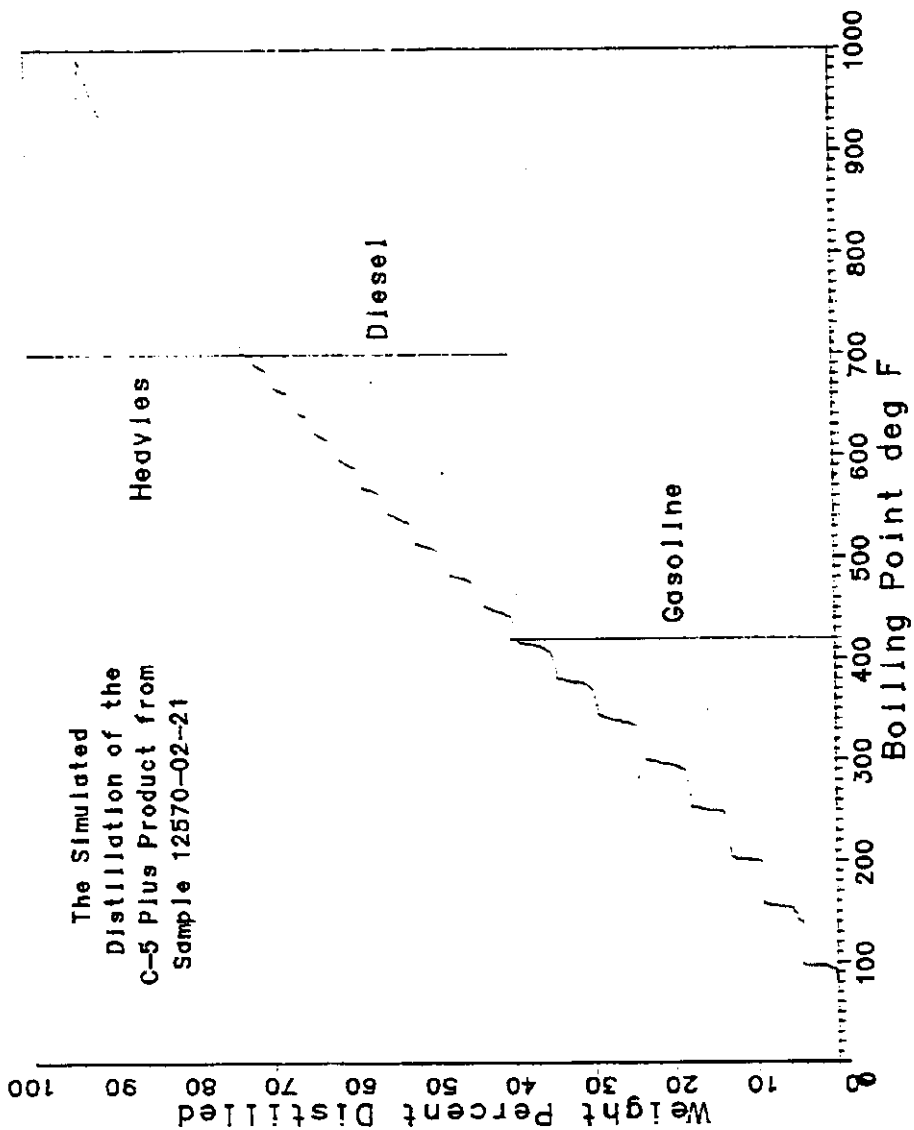


Fig. B35

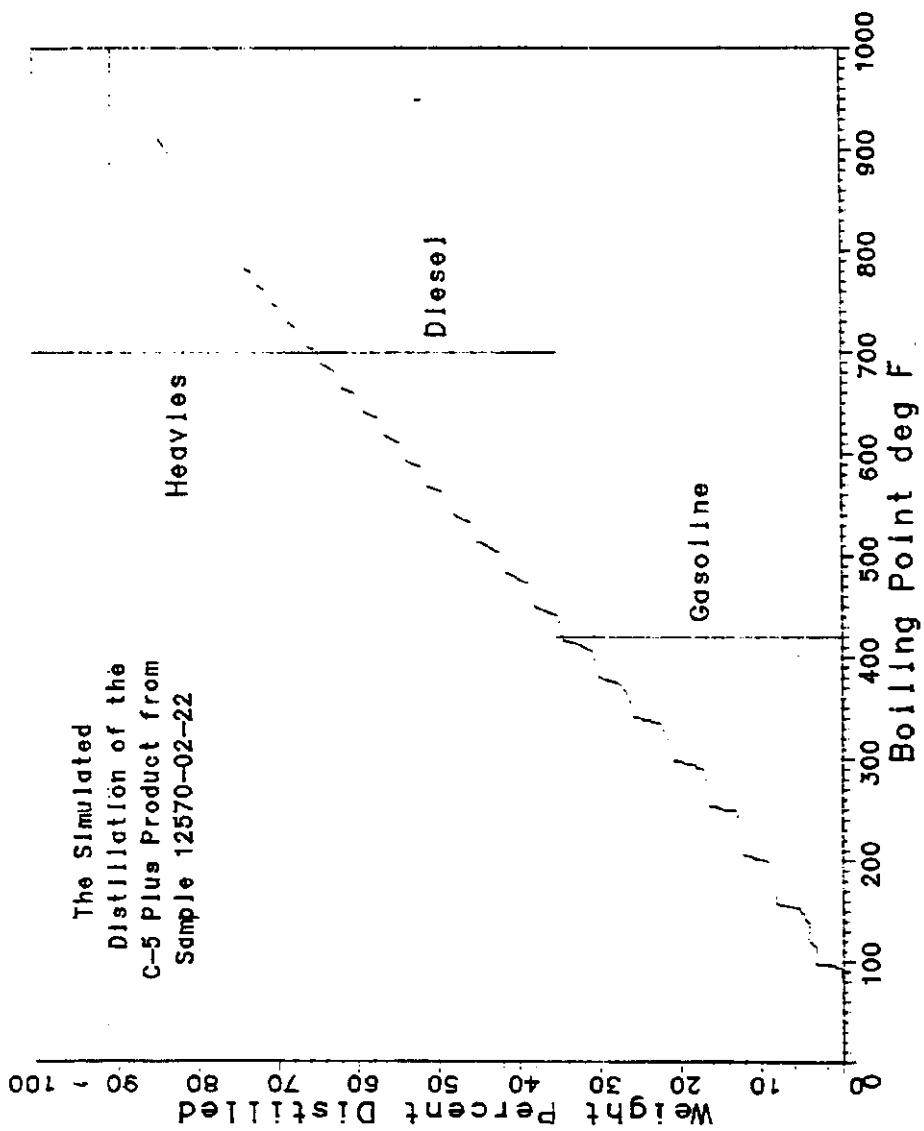


Fig. B36