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SIMULATED DISTILLATION OF COAL-DERIVED LIQUIDS

by

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ABSTRACT

Simulated distillation using the gas chromatographic technique was attempted in this study in order to obtain boiling range distribution curves for two petroleum liquids and eight coal-derived liquid samples. The simulated distillation procedure is discussed in detail and the boiling range distribution curves, as well as the ASTM D-86 distillation curves, were reported for each petroleum liquid and each coal-derived liquid under study.

Comparison of the results obtained from this study has been done with the actual data obtained from Marathon Oil Company laboratories and with actual data obtained from other distillation techniques.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF TABLES

LIST OF TABLES (cont.)

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DEDICATION

TO MY PARENTS FOR THEIR ENCOURAGEMENT, TO MY WIFE FOR HER UNDERSTANDING AND TO MY SON AYMEN FOR HIS SMILING NATURE.

بسم الله الرحمن الرحيم

IN THE NAME OF GOD MOST MERCIFUL

AND MOST COMPASSIONATE

INTRODUCTION

The SRC processes which are used to convert coal into distillate products involve conversion and separation steps that operate at high temperatures and pressures. The design of these processing steps for large-scale coal liquifaction plants requires a knowledge of the physical, chemical and thermodynamic properties of coal liquid fractions.

Coal liquids generally boil over a very wide range of temperatures and contain so many chemical compounds that the only practical way to characterize their composition is to fractionate the coal liquid into narrow boiling cuts. These cuts can be specified by their boiling point distribution, using such separation techniques as distillation, gradient elution chromatography, acid and base extractions, and gel permeation chromatography (1,2).

Many conventional laboratory distillation methods are used to obtain these boiling point distributions (3). The most widely used methods are ASTM D-86 and the reduced pressure equivalent ASTM D-1160. Despite the fact that these methods are rapid one-plate distillations, and capable of fair precision, the data obtained bear little relation to the true boiling point distribution of the sample (4,5).

In 1971 an ASTM D-2893 standard method was published; the method employed a column with an efficiency of 15 theoretical plates. However, the analysis time of this method was found to be very long (6).

The determination of boiling range characteristics for petroleum fractions or coal-derived liquids by gas chromatography has gained rapid acceptance since the publication of ASTM D-2887 in 1973. This gas chromatographic method provides superior precision and more detailed information than can be achieved using the two conventional ASTM distillation methods D-86 and D-1160. The ASTM D-2887 was found to be applicable to all petroleum fractions boiling between 100^{o}F and 1000^{o}F (7).

Simulated distillation is a gas chromatographic technique that has been applied within the petroleum industry to obtain true boiling point distributions for petroleum fractions, but the technique has not been applied widely on coal-derived liquid. In this study, the simulated distillation technique is used on both coal-derived liquids and petroleum fractions to see how this method can be applied on coal-derived liquids. Several authors have discussed future applications of the simulated distillation technique (8,9).

Objectives of This Study

The objectives of this study are:

1. To apply the simulated distillation technique using gas liquid chromotography in order to determine boiling range distribution data which is widely used for coal liquid characterization.
2. To find a link between the simulated distillation method and other experimental ASTM distillation methods.

Principles of the Simulated Distillation Method

When a sample of hydrocarbons is injected into a suitable non-polar liquid phase gas chromatographic column of restricted efficiency, the hydrocarbons will separate in boiling point order. This fact is the basis for simulated distillation. The column temperature should be programmed upward at a reproducible rate to effect the elution of the sample being used.. The temperature programming must start below the initial boiling point and end after the sample is totally eluted.

An automatic integrating device which has the capability of measuring peak area slices at a certain time interval must be used to collect the required data. To determine true boiling point distributions, an area slice program must be used. The area slices are a measure of the amount of the sample eluted or separated from the column at a certain time interval. The area of each slice is recorded at timed intervals throughout the run, and the total number of peak area slices are summed to obtain a total area count. Area percentages are calculated for each time interval in order to determine true boiling point distributions by dividing each area count by the total area count (10).

A normal hydrocarbon mixture supplied by Hewlett-Packard Company is used as a standard mixture to generate

the calibration curve from which the sample boiling range distribution can be determined. The standard mixture of normal hydrocarbons should cover the entire boiling range of the samples to be analyzed.

The calibration curve is generated by injecting the normal paraffin standard under identical sample conditions, and the area percent data is calculated. The known boiling point of each component in the standard mixture is assigned to its retention time. A retention time vs. boiling point can be plotted and used to calculate the boiling point distributions for the samples under study.

Definitions

Initial boiling point (IBP) can be defined as the point at which the cumulative area count is equal to 0.5 percent of the total area under the chromatogram.

Final boiling point (FBP) can be defined as the point at which the cumulative area count is equal to 99.5 percent of the total area under the chromatogram.

Retention time is the time a component can take for a complete elution, and it can be measured from injection to the apex of the component's peak.

Gas Chromatography

Gas chromatography is a physical separation of two or more components based on their differential distribution between two phases. One of them is a stationary phase and the other is a gas phase (11).

The chromatograph employs a carrier gas or mobile phase under pressure to move a vapor sample from the injection port through a stationary phase where separation takes place, to a detector where the sample is converted to an electrical signal. The signal is then measured by the strip chart recorder (12). Basic components of a gas chromatograph are shown in Figure 1.

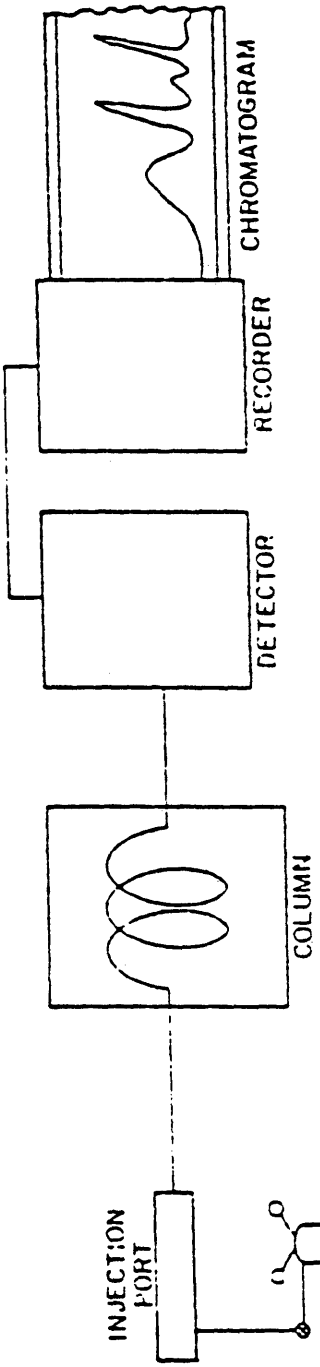

FIG. 1 BASIC COMPONENTS OF A GAS CHROMATOGRAPH

Instrument Description used for Simulated Distillation

A Hewlett-Packard 5710 A gas chromatograph was used for all samples for which simulated distillation was required. A brief description for each component of the gas chromatograph follows:

Column

The column is the most important part in any gas chromatograph, and it is composed of three elements: the metal or glass tubing, the solid support, and the stationary phase.

The metal or glass tubing does not affect the chromatographic separation; common materials used are stainless steel, copper or glass. Most gas chromatographic columns are made of stainless steel because of the combination of desirable properties it provides. Two stainless steel GC columns have been used in this study; each column was 1/4 inch in diameter and 3 feet long. The two columns were packed with 100/200 mesh chromosorb 'W' coated with 10 percent UCW 982 liquid phase. The gas chromatograph was operated under the differential mode to compensate for base line drift (12,13).

Detector

Either a thermal conductivity or a flame ionization detector can be used for this kind of analysis. A flame ionization detector has been used in this study. The operating principle of the FID can be summarized as follows: when the effluent gas from the column is mixed with hydrogen and burned in air or oxygen, ions or charged particles are produced. These ions enter the electrode gap, and decrease the gap resistance; thus a current is permitted to flow in the external circuit and this current is amplified by an electrometer.

The FID is a selective unit in the GC. It will respond only to the materials which produce ions when they are burned. It ignores many compounds such as water, nitrogen, and carbon dioxide. Selectivity is a very desirable thing, and aqueous samples can be analyzed using FID without a huge solvent peak eluting in the first part of the chromatogram. The FID performance depends on the proper choice of gas flow rates, and the response of the FID is a sensitive function of hydrogen flow rate. In general, good sensitivity and stability are obtained with a hydrogen flow rate of 30 ml/min, air flow rate of 300 ml/min, and carrier gas flow rate of 40 ml/min.

Sample Inlet System

The liquid samples must be introduced clean into the moving gas stream at a pressure and temperature above the ambient through the septum and injection port. The injection port is a metal block containing heaters, with a septum holder on the front and a connection for the column on the rear. There is a capillary glass tube inside the injection port in which the carrier gas is preheated. The injected sample is flash vaporized in the injection port and it entered the carrier gas flow. The primary purpose of the injection port is to convert the liquid sample into a vapor phase. This process requires that the injection port be heated so that the sample is flash vaporized as quickly as it is injected by the syringe. It is recommended that the injection port temperature be above the boiling point of the highest component in the sample, but nobody can predict what this boiling point is, or even what the highest boiling component is. So the injection port temperature can be set to a higher temperature or maximum temperature of the column (14,15).

Integrator

The integrator is an automatic device which was used to measure the accumulated area under the chromatogram, as well as the retention time at the specified time intervals

for the samples whose simulated distillation is required. A Hewlett Packard 3385 A automatic integrator was used in this study. This device was also used to determine the retention time for each component in the calibration mixture to construct the calibration curve.

Recorder

A strip chart recorder was used for the qualitative studies only, as in the determination of the retention time of the standard mixture. The strip chart is divided into inches, and its speed can be regulated to move at 1.0 min/inch or 0.25 min/inch.

Instrument Operation and Operating Conditions

In order to obtain correct true boiling point data, the standard and each sample must have identical operating conditions. The chromatograph is temperature programmed immediately after sample injection into the GC column. The initial column temperature was selected to be -20°C. Carbon dioxide liquid was used as a coolant medium to bring the column temperature down to -20°C. This temperature is held constant for two minutes, then the column temperature is increased at a reproducible rate of 8°/min until the temperature reaches 360°C; and finally this temperature is held constant for some time until the entire sample is totally eluted. As the temperature programming takes place, the area slice measurements using the automatic integrator must be recorded. The automatic integrator starts area slice measurement after 0.5 minutes of sample injection. The area slice summations are taken at 0.5 minute increments until summation ends after the sample is totally eluted. The gas chromatographic conditions and column specifications, as well as gas flow rates, are shown on Table 1.

TABLE 1

GAS CHROMATOGRAPH OPERATING CONDITIONS

Chromatograph: HP 5710 A Gas Chromatograph	
Injection port temperature	300°C
Detector temperature	350°C
Initial oven temperature	-20°C
Time at initial temperature	2 min
Heating rate	8 deg C/min
Final oven temperature	360°C
Detector	Flame ionization detector
Column length	3 feet
Column diameter	1/4 inch
Liquid phase	10% UCD-W982
Support mesh size and material	100/120 mesh chromosorb W
Sample size	1μℓ
Helium flow rate	60 ml/min
Air flow rate	240 ml/min
Hydrogen flow rate	30 ml/min
Integrator slope sensitivity	0.05

Instrument Calibration

The most important step of the simulated distillation method is instrument calibration. The calibration was done by injecting a known boiling point mixture, (supplied by Hewlett-Packard and containing nineteen normal paraffin components), and recording the retention times of the various components in this standard mixture. The operating conditions, the injection port temperature, the detector temperature, and the gas flow rates must be identical to the operating conditions used for all samples under study. The recorded retention times obtained from the normal paraffin mixtures vs. the known boiling points of each component are plotted on a linear graph to relate time from injection to the actual boiling point of each component in the mixture. This calibration curve is shown in Figure 2, and the data obtained to construct this calibration is shown in Table 2.

Many gas chromatographic runs were made on the standard mixture for two purposes: first, to check the reproducibility of the system by obtaining concentration data of this standard mixture, and second, to compare this data with the actual concentration data obtained from Hewlett Packard Company. The actual concentration data and the calculated concentration from the gas chromotrgraph are compared and reported in Tables 3 and 4.

TABLE 2

RETENTION TIMES AND BOILING POINTS FOR THE NORMAL PARAFFIN HP STANDARD MIXTURE

Carbon No.	Retention Time,* Min	Boiling Point °F
5	6.12	97
6	9.29	156
7	11.99	209
8	14.43	258
9	16.67	303
10	18.68	345
11	20.69	385
12	22.39	421
14	25.74	488
15	27.29	519
16	28.71	548
17	30.09	576
18	31.39	602
20	33.78	651
24	37.98	736
28	41.56	809
32	44.69	874
36	47.47	928
40	49.97	977

*The retention time is the average of at least three runs.

TABLE 3

ACTUAL CONCENTRATIONS OF THE VARIOUS COMPONENTS IN THE NORMAL PARAFFIN HP STANDARD MIXTURE

Carbon No.	B.Pt °F	Volume, ml	Weight, g	Weight percent
5	97	30	-	8.562
6	156	7.5	-	2.253
7	209	15	-	4.669
8	258	15	-	4.795
9	303	15	-	5.100
10	345	30	-	9.963
11	385	15	-	5.050
12	421	60	-	20.425
14	488	30	-	10.404
15	519	15	-	5.239
16	548	30	-	10.547
17	576	15	-	5.304
18	602	-	5	2.262
20	651	-	3	1.357
24	736	-	2	0.905
28	809	-	2	0.905
32	874	-	2	0.905
36	928	-	2	0.905
40	977	-	1	0.452

TABLE 4

COMPARISON BETWEEN THE CONCENTRATION OBTAINED FROM THIS STUDY AND THE CONCENTRATION OBTAINED FROM HP FOR THE NORMAL PARAFFIN HP STANDARD MIXTURE

Carbon No.	Actual Concentration Wt %	Calculated Concentration(this study)Wt.%
5	8.562	8.575
6	2.253	2.443
7	4.669	4.799
8	4.795	4.386
9	5.100	4.755
10	9.963	9.773
11	5.050	4.873
12	20.425	20.777
14	10.404	10.830
15	5.239	5.240
16	10.547	10.767
17	5.304	5.304
18	2.262	2.191
20	1.357	1.338
24	0.905	0.877
28	0.905	0.899
32	0.905	0.880
36	0.905	0.923
40	0.452	0.387

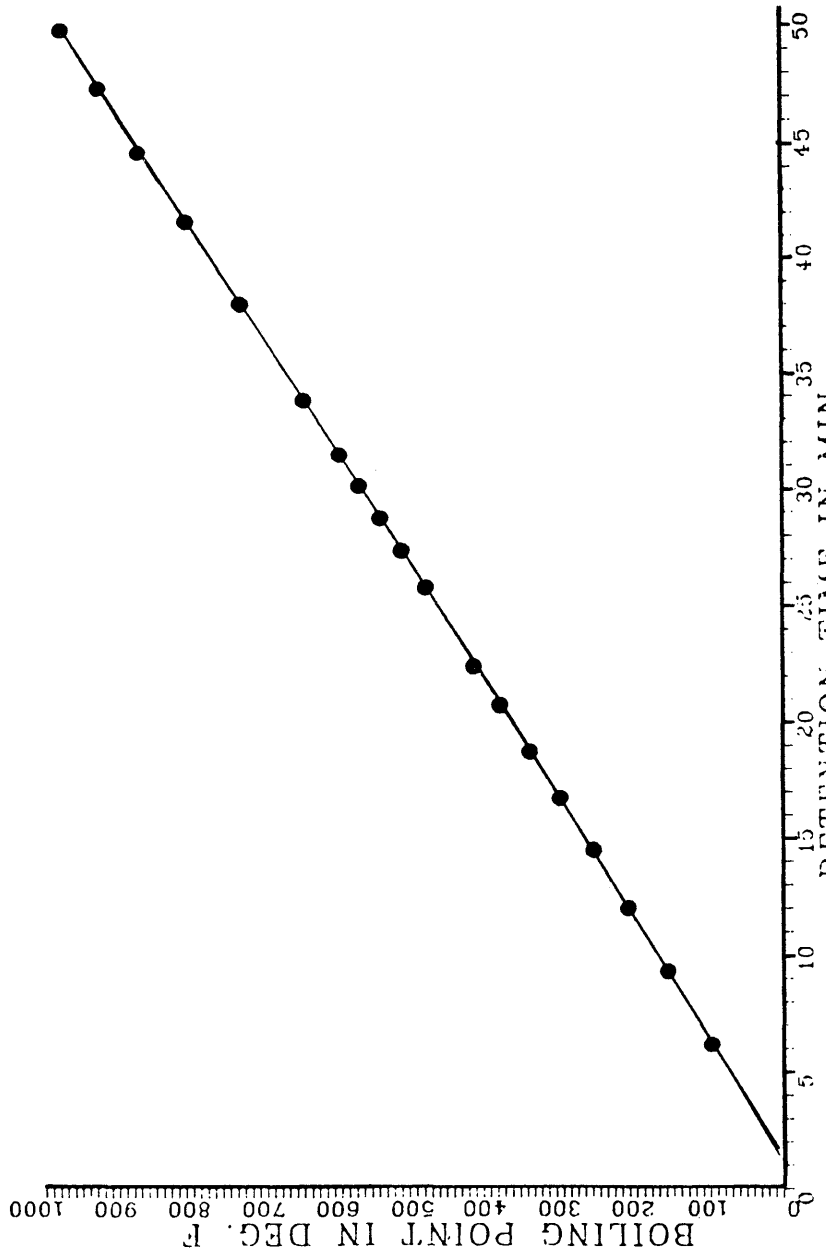

FIG. 2 BOILING POINT VS RETENTION TIME FOR THE HEWLETT PACKARD NORMAL PARAFFIN STANDARD (CALIBRATION CURVE)

SAMPLE LIST

The coal-derived liquids used in this study were produced by one of three processes: char-oil energy development (COED), synthoil or solvent refined coal (SRC). A complete listing of all samples studied and a brief description is given below:

1. Eugene Island Well
2. ASTM Reference Gas Oil Liq #1
3. 1046 Naphtha
4. SRC II-500 Cut
5. SRC II-600 Cut
6. SRC I- Naphtha
7. '878' Middle Distillate
8. Utah Light Distillate
9. Western Kentucky Light Distillate
10. Synthoil

Sample Descriptions

The Eugene Island well and ASTM reference gas oil samples are two petroleum fractions; they were supplied by Marathon Lab.

The SRC II-500 and SRC II-600 cuts are narrow boiling range distillation cuts. The two cuts are from Gulf Research and Development Company.

The western Kentucky light distillate is obtained from distillation performed on western Kentucky whole oil, which is a syncrude produced by the COED process at the P&M DuPont, Washington, plant.

The Utah light distillate is a coal-derived liquid produced after distillation was performed on the whole oil. The original oil was received from P&M and produced by the COED process under certain conditions using a Utah coal.

The SRC-I naphtha is a distillate received from P&M. It came from a whole oil made by the SRC process on a Kentucky coal. The SRC process uses a pressure of 1260 psig and a temperature of 455 ^{o}C.

Both 1046 naphtha and '878' middle distillates are distillates from oils obtained by the SRC II process.

The original synthoil was produced by P&M by the synthoil process. This process is carried out in a fixed bed reactor with a 35% coal slurry. The slurry flows at 25 lb/hr under a pressure of 4000 psig and temperature of 450 ^{o}C. The slurry is made from a West Virginia coal. To get the synthoil light, the oil is distilled by a process similar to that used to obtain the western Kentucky light.

Experimental Procedure:

The experimental procedure used to generate true boiling point distributions for the samples under study can be summarized according to the following steps:

Step 1

The Gas Chromatographic column must be conditioned and it should be in a fresh condition before any analysis can be done, then the flow rate of the carrier gas which passes through the column and the detector jets must be measured using the soap film flow meter and a stop watch. This process must be done before turning any temperature switch on, to avoid any error in the flow rate due to gas expansion.

Step 2

The injection port, detector, and oven temperatures should be turned on at the desired settings, as mentioned in Table 1. Also the hydrogen and air flow rates must be adjusted to the proper ratios, which are dependent upon the carrier's gas flow rate and column specifications. Then the flame ionization detector should be ignited by pressing the ignitor for a few seconds over the detector exit vent. The appearance of condensation on a glass mirror when held close to the detector exit is an indication that the flame is lit.

Step 3

The column must be cooled down to the starting temperature by lowering the oven temperature to -20°C using carbon dioxide liquid at the exact time the desired volume of the sample is injected, using a 10 µL syringe. Immediately, the temperature programming must be started upward at the desired rate that will produce sample separation.

Step 4

The recorder chart drive and the automatic integrator also must be turned on immediately after injecting the sample. As soon as the column temperature starts to increase, the separation will take place at the selected sensitivity. The separation is detected by the detector and recorded in the form of peaks. The automatic integrator will integrate the area under the chromatogram continuously according to an area slice program selected before sample injection. The integration must start after injection and must end as the sample is totally eluted, which is indicated by reaching a steady base line. The automatic integrator will quit integration automatically or manually at the end of the run.

Step 5

At the end of the run, the automatic integrator will print a report indicating the retention time intervals, cumulative area counts, and area percentages. The area

percentages were obtained automatically by dividing the cumulative area count at each interval by the total cumulative area counts. The percent of sample distilled or recovered at any time interval is equivalent to the cumulative area percent at the same time interval. The cumulative area percentages were found by summing the area percentages corresponding to each time interval. The initial boiling point can be found corresponding to 0.5 percent of cumulative area, and the final boiling point can be found corresponding to 99.5 percent of cumulative area (16,17).

Step 6

The cumulative area percentage or the percent distilled for each sample at each time interval can be tabulated and the boiling temperature can be assigned to that time interval from the calibration curve (Fig. 2).

Therefore, the true boiling point distillation data can be found for each sample, and a TBP distribution curve for each sample can be constructed by plotting each boiling temperature against its corresponding percent of sample distilled or recovered.

Comparison of Simulated Distillation Data

The Marathon Research Lab in Denver did a simulated distillation on the Eugene Island well and the ASTM Reference gas oil samples in order to obtain TBP distribution data. The simulated distillation has been done on these two petroleum fractions by this study in order to note the overall accuracy of the simulated distillation method. The TBP distribution data obtained is compared with the TBP distribution data from Marathon Lab. The comparison of the results is shown in Tables 5 and 6. It should be noted that the Marathon data and the data obtained from this study are calculated according to the same standard which is the normal paraffin mixture, a fact that does not cause any discrepancies between the two data sets except in the initial and final boiling points. The Marathon simulated distillation data is more accurate in obtaining the initial and final boiling points because of using lower boiling point normal paraffin compounds in addition to the normal paraffin standard; hence, the calibration curve can be extended to include lower boiling points.

The Hauser laboratories in Boulder did the simulated distillation on SRC II-600, SRC II-500 middle distillates and 1046 Naphtha. The TBP distributions obtained are compared with the SIMDIS TBP distributions from this study for each sample. The comparisons are in the form of curves

and data points and they are shown in Figures 5,6,7 and Tables 7,8,9. The simulated distillation TBP data for both the 1046 Naphtha and the SRC II-600 sample does not give good agreement with the TBP data obtained from Hauser Lab. A possible reason for this discrepancy is the increased amounts of heteroatomic and aromatic compounds in such coal-derived liquids. The SIMDIS TBP data for SRC II-500 sample is slightly higher than the TBP data from Hauser Lab. The difference between the two data points does not exceed 10 degrees.

The ASTM D-86 distillation was performed on 1046 Naphtha, SRC-I Naphtha,"878"middle distillate, western Kentucky light distillate, Utah light distillate and synthoil samples at Colorado School of Mines. The actual ASTM D-86 distillations obtained was reported by several authors (18,19,20). The simulated distillation technique was used on the same samples. The SIMDIS TBP results are reported and converted to the ASTM D-86 distillation data using the correlation in the API Technical Data Book (21). The converted or calculated ASTM D-86 distillations are compared with the actual ASTM D-86 distilaltions. The comparisons are in the form of curves and data points. These comparisons are illustrated in Figures 3 through 13 and Tables 10 through 15.

From these comparisons, it is obvious that the simulated distillation distributions have higher boiling points than the ASTM distillation distributions. This behavior can be caused by the higher aromatic and hetero-atomic contents which such coal liquids have compared with a petroleum fraction of the same boilng point range. Another reason for data deviation might be caused from the GLC-simulated distillation apparatus which was de-signed for mass production analysis of petroleum samples. Consequently, the simulated distillation results were very poor as compared with other distillations such as ASTM D-86 distillation which is based on volumetric analysis.

TABLE 5

COMPARISON OF SIMDIS TBP DISTRIBUTION WITH TBP DISTRIBUTION DONE BY MARATHON LAB FOR EUGENE ISLAND WELL

Percent Distilled	TBP °F SIMDIS	TBP °F Marathon Lab.
IBP	90	10
10	220	221
20	293	286
30	368	348
40	432	424
50	490	488
60	552	548
70	612	606
80	678	672
90	752	745
FBP	904	895

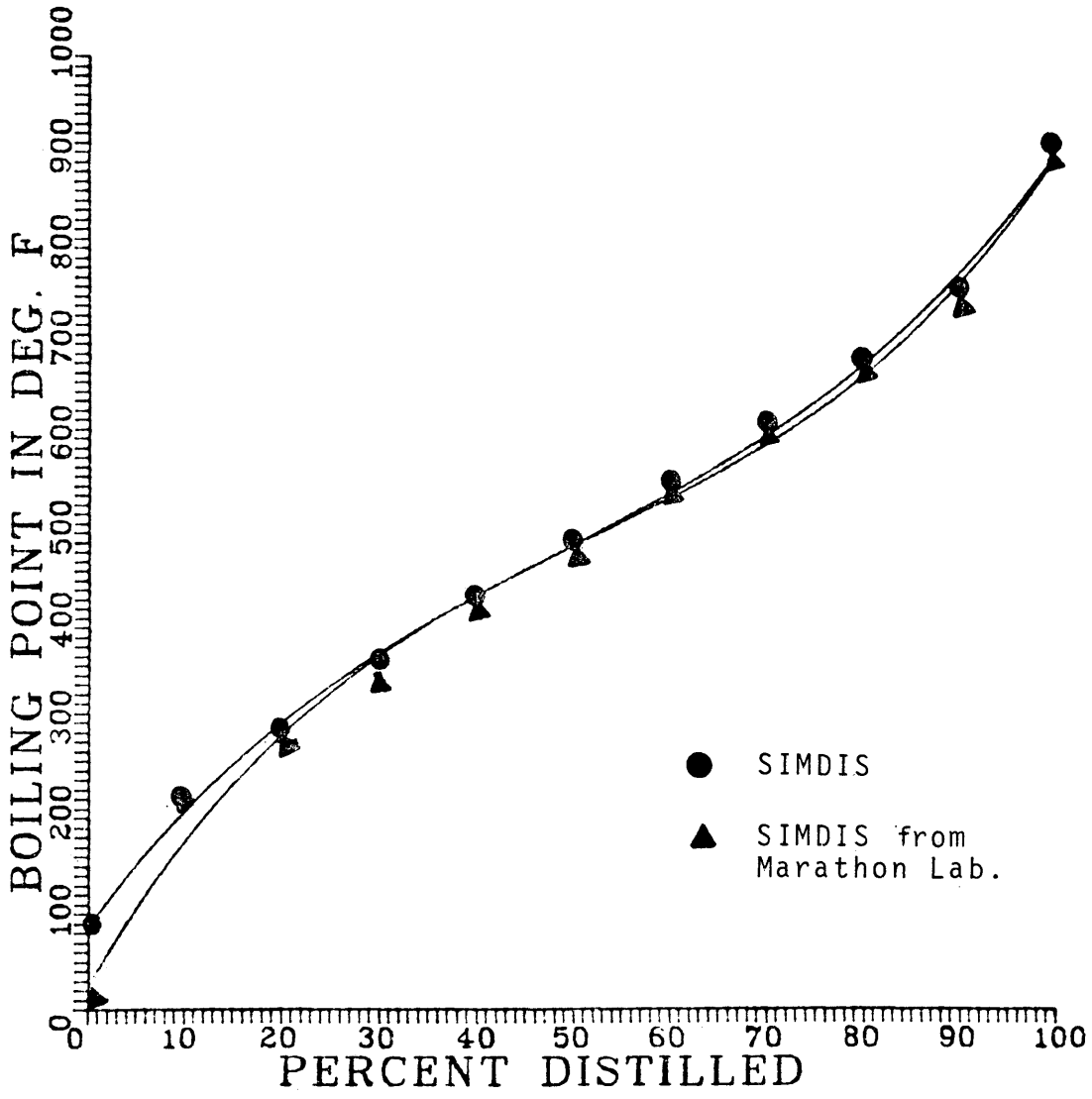

Fig. 3 COMPARISON OF SIMDIS TBP DISTRIBUTION WITH SIMDIS TBP DISTRIBUTION FROM MARATHON LAB. FOR EUGENE ISLAND WELL

TABLE 6

COMPARISON OF SIMDIS TBP DISTRIBUTION WITH THE TBP DISTRIBUTION DONE BY MARATHON LAB FOR ASTM REFERENCE GAS OIL #1

Percent Distilled	TBP °F SIMDIS	TBP °F From Marathon Lab
IBP	225	238
10	340	336
20	435	429
30	505	496
40	555	548
50	595	594
60	732	629
70	672	669
80	710	709
90	760	759
FBP	882	887

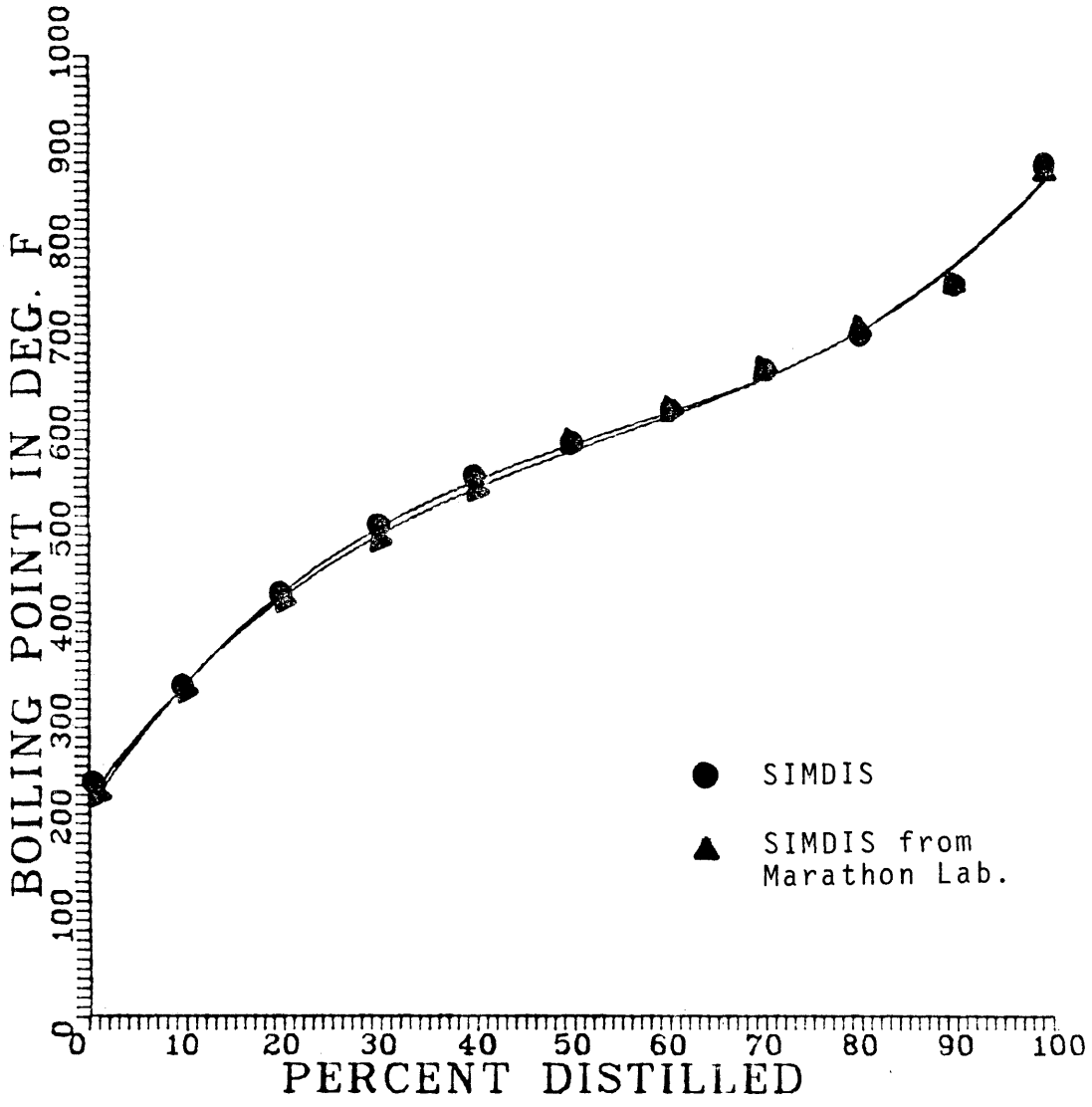

Fig 4. COMPARISON OF SIMDIS TBP DISTRIBUTION WITH SIMDIS TBP DISTRIBUTION FROM MARATHON LAB FOR ASTM REFERENCE GAS OIL #1

TABLE 7

COMPARISON OF SIMDIS TBP DISTRIBUTION WITH TBP FROM HAUSER LAB FOR 1046 NAPHTHA

Percent Distilled	TBP °F SIMDIS	TBP °F from Hauser Lab.
IBP	128	60
10	186	170
20	220	185
30	245	215
40	265	230
50	275	250
60	310	275
70	328	310
80	347	325
90	378	355
FBP	470	410

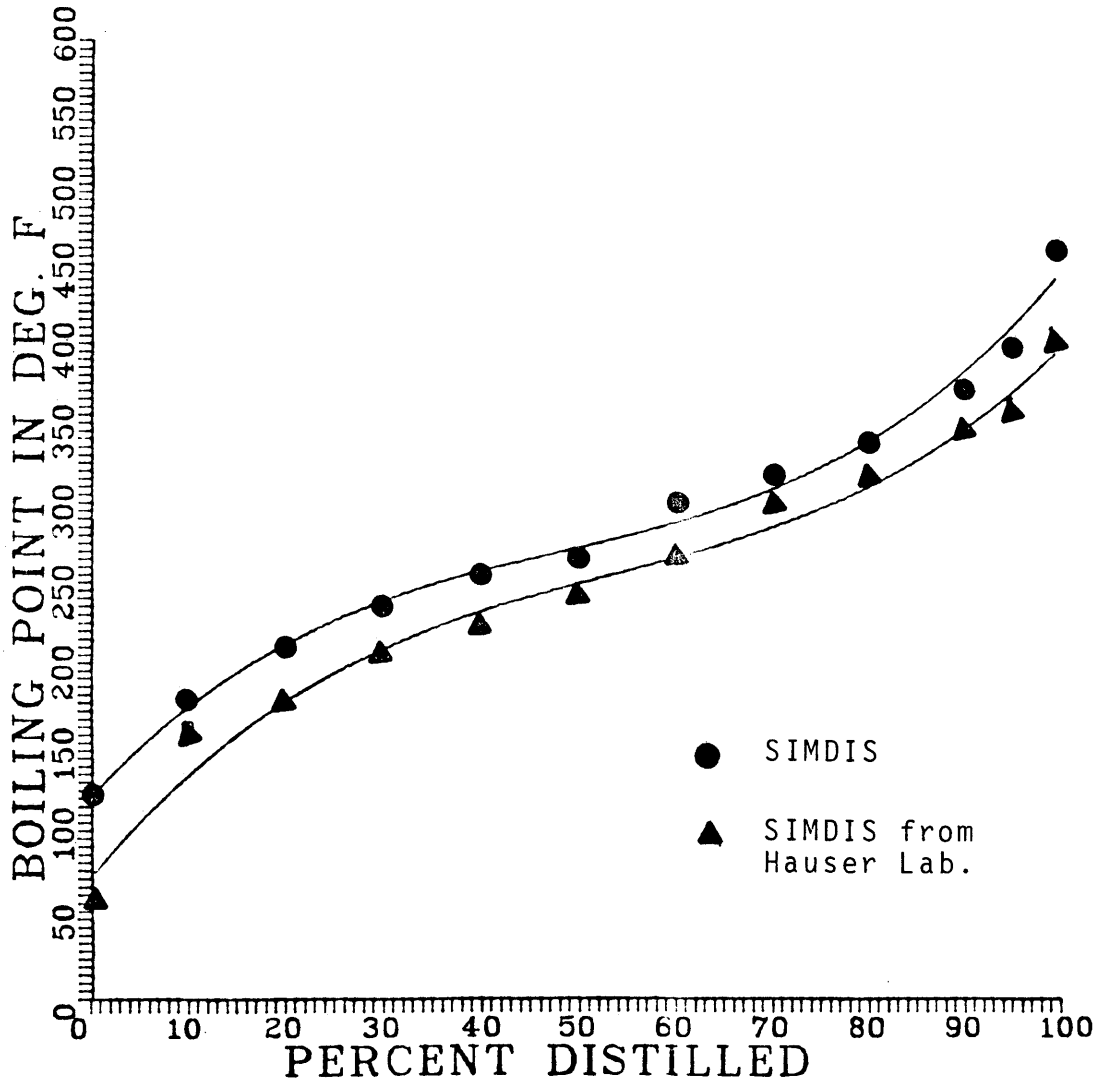

Fig. 5 COMPARISON OF SIMDIS TBP DISTRIBUTION WITH SIMDIS TBP DISTRIBUTION FROM HAUSER LAB. FOR 1046 NAPHTHA

TABLE 8

COMPARISON OF SIMDIS TBP DISTRIBUTION WITH TBP DISTRIBUTION FROM HAUSER LAB FOR SRC II-500 CUT

Percent Distilled	TBP °F SIMDIS	TBP °F from Hauser Lab.
IBP	367	355
10	425	425
20	450	445
30	470	460
40	486	475
50	500	490
60	513	505
70	525	515
80	545	530
90	570	545
100	625	580

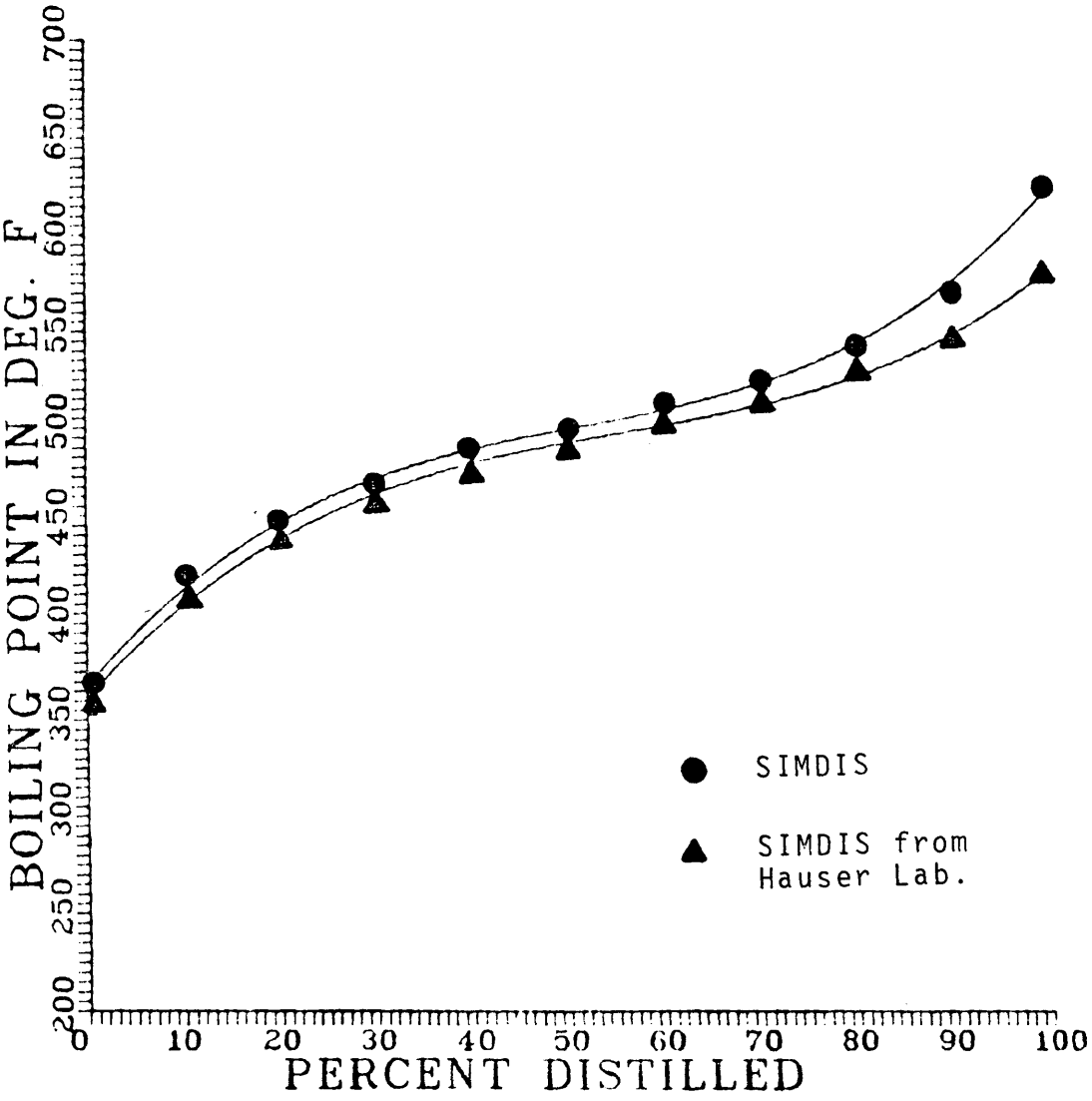

Fig. 6 COMPARISON OF SIMDIS TBP DISTRIBUTION WITH TBP DISTRIBUTION FROM HAUSER LAB FOR SRC II 500 CUT

TABLE 9

COMPARISON OF SIMDIS TBP DISTRIBUTION WITH TBP DISTRIBUTION FROM HAUSER LAB FOR SRC II-600 CUT

Percent Distilled	TBP °F SIMDIS	TBP °F Hauser Lab
IBP	485	490
10	548	535
20	568	540
30	580	555
40	596	565
50	605	575
60	612	580
70	618	590
80	628	595
90	648	605
FBP	700	660

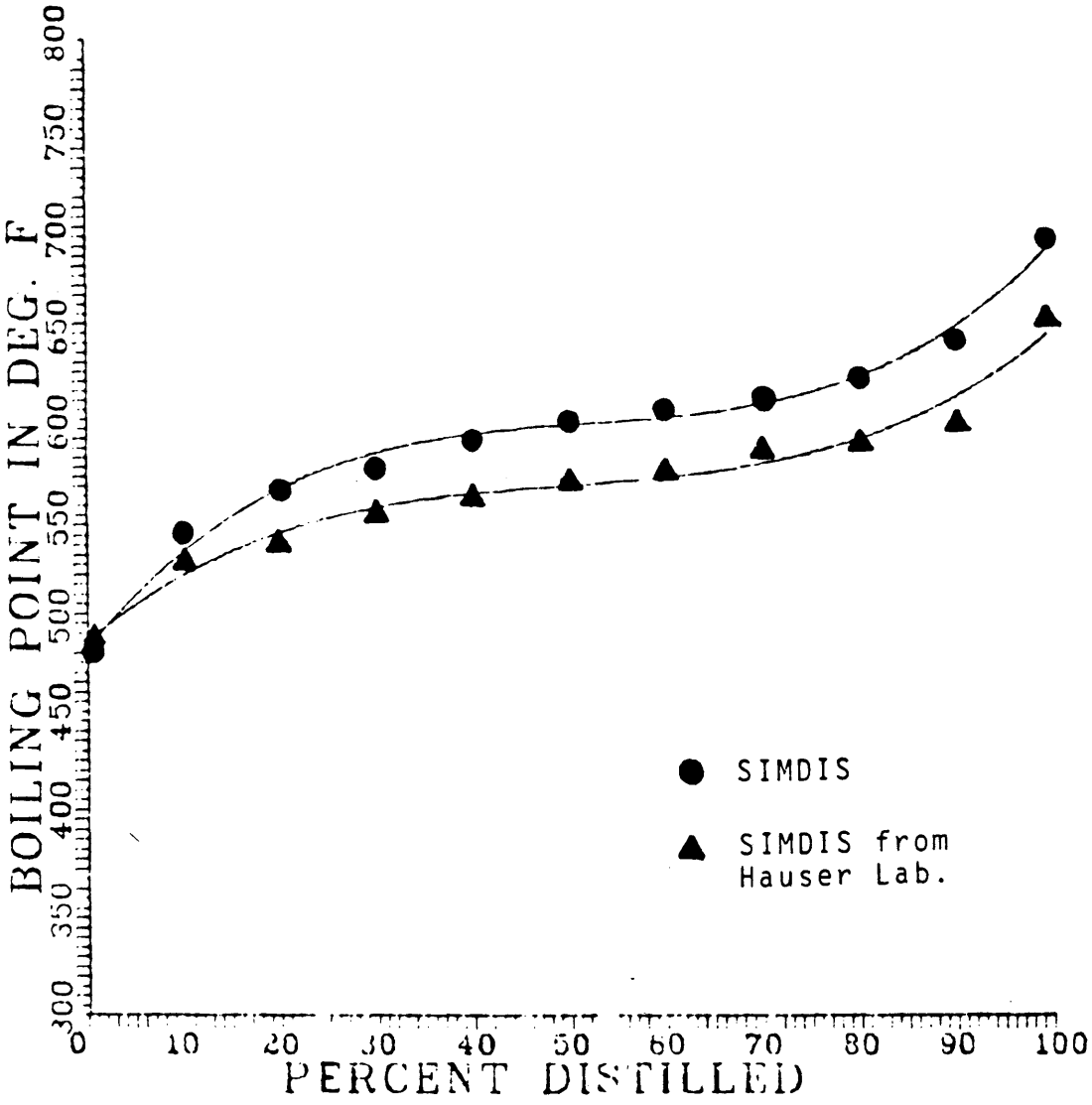

Fig. 7 COMPARISON OF SIMDIS TBP DISTRIBUTION WITH SIMDIS TBP DISTRIBUTION FROM HAUSER LAB FOR SRC II-600 CUT

TABLE 10

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR 1046 NAPHTHA

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual ASTM D-86 Temp. °F
IBP	195	150
10	228	193
20	250	224
30	263	242
40	272	256
50	280	275
60	295	293
70	319	312
80	330	335
90	353	362
95	380	406
FBP	438	413

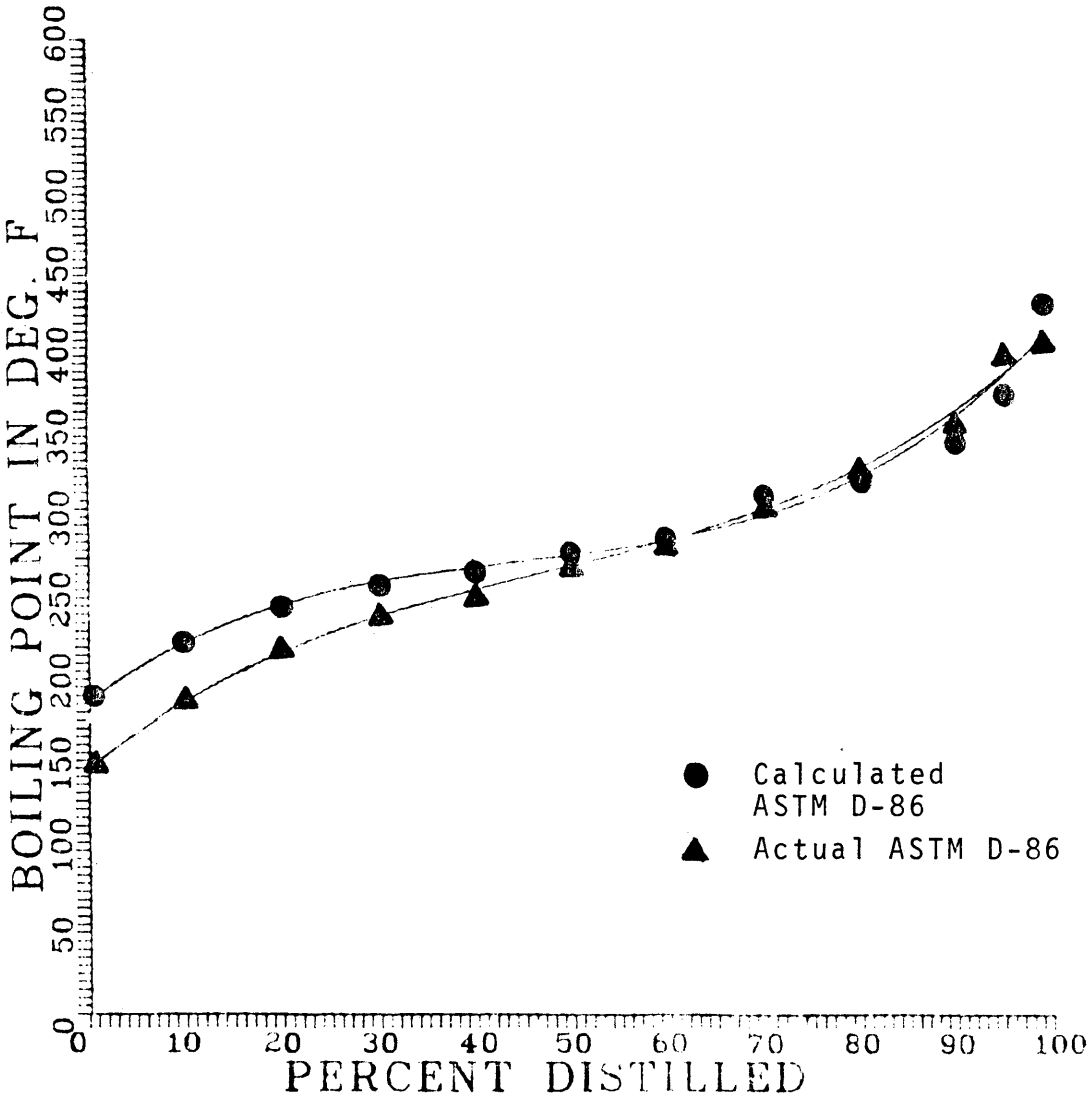

Fig. 8 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR 1046 NAPHTHA

TABLE 11

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR THE SRC-1 NAPHTHA

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual D-86 Temp. °F
IBP	209	138
10	237	180
20	250	194
30	260	205
40	272	216
50	285	229
60	295	246
70	311	266
80	329	287
90	350	325
FBP	442	373

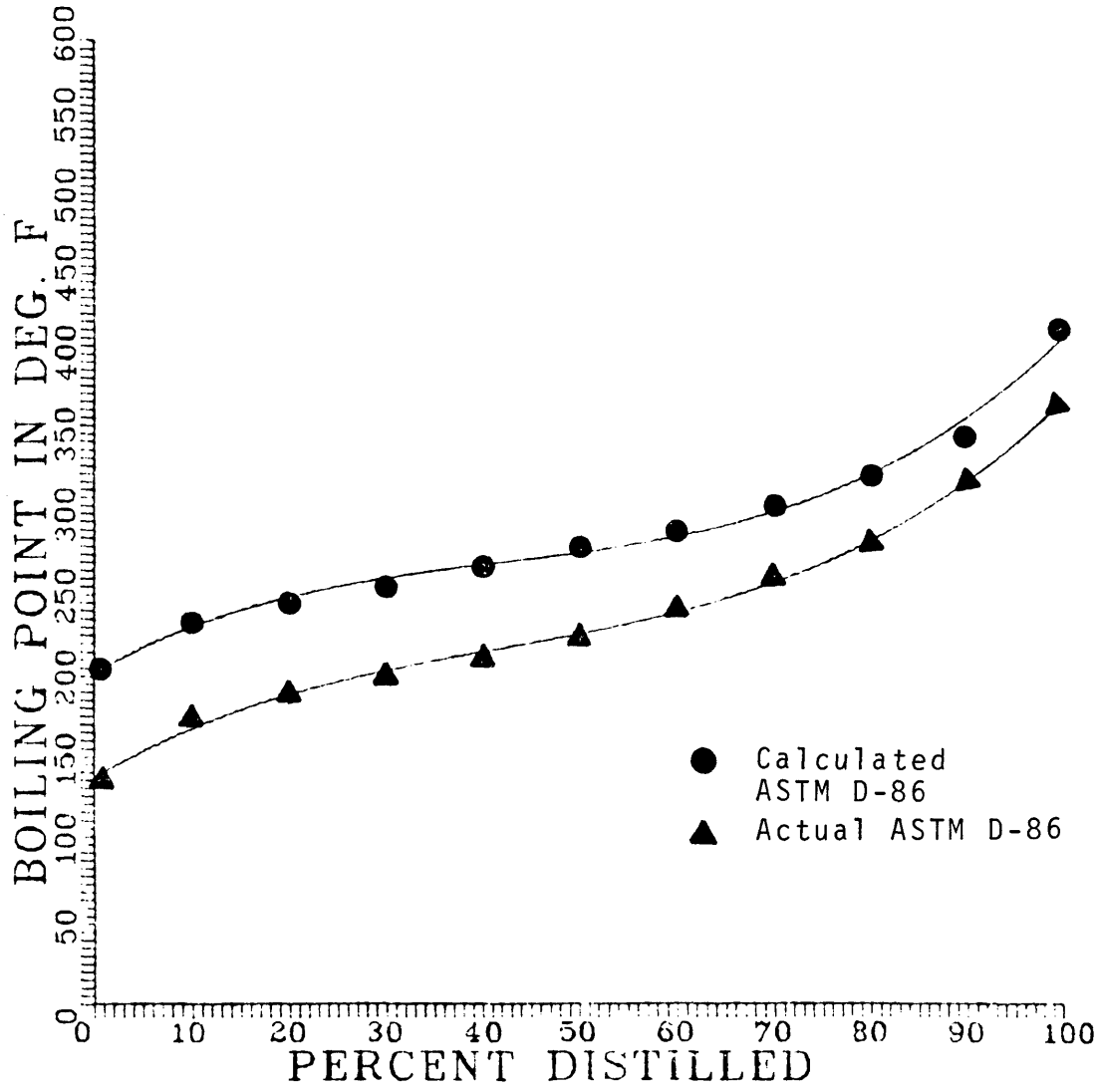

Fig. 9 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR SRC-I NAPHTHA

TABLE 12

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR '878' MIDDLE DISTILLATE

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual ASTM D-87 Temp. °F
IBP	356	354
10	409	400
20	415	413
30	425	418
40	437	428
50	448	437
60	465	445
70	478	456
80	490	468
90	503	485
FBP	553	532

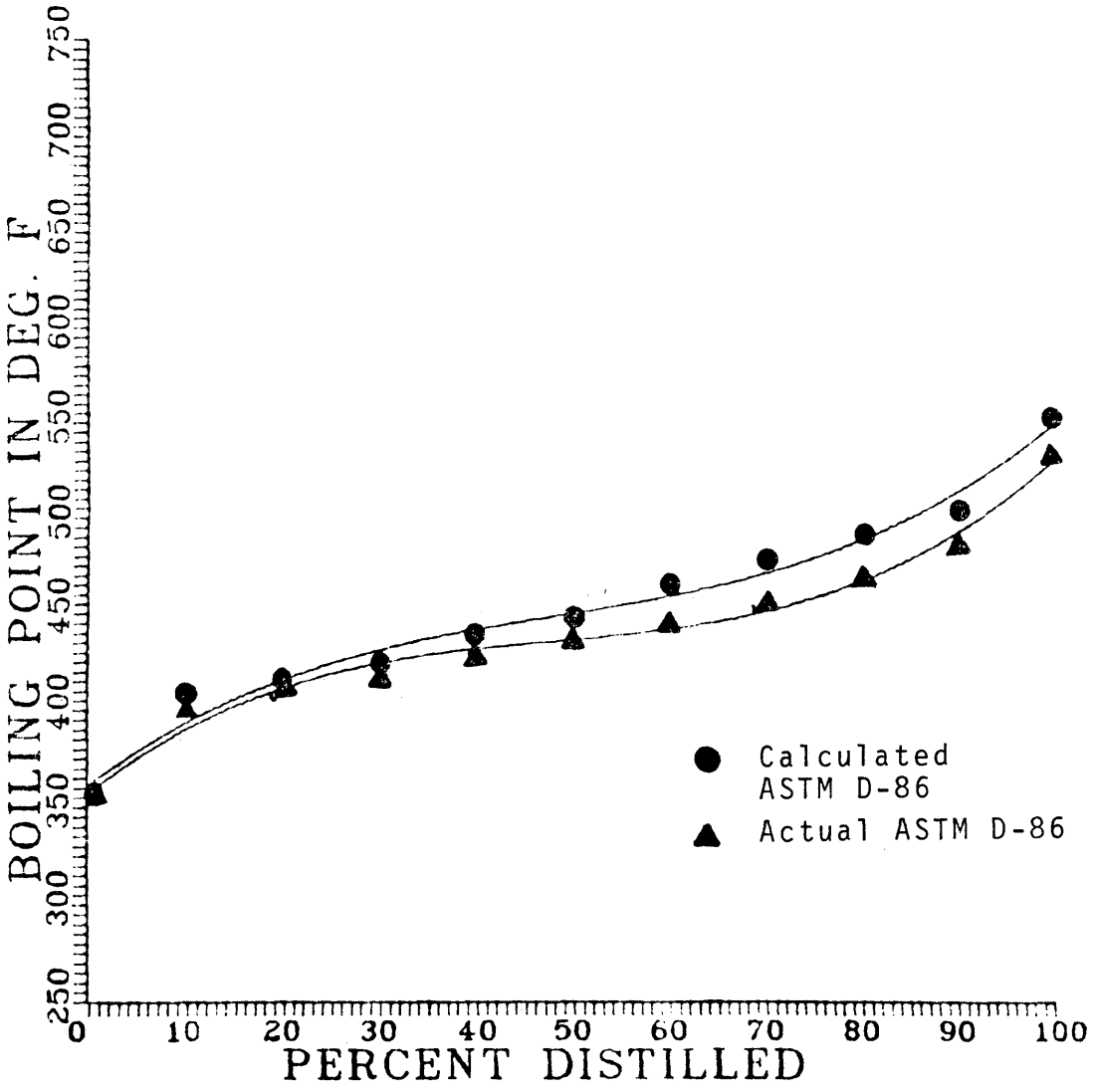

Fig. 10 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR '878' MIDDLE DISTILLATE

TABLE 13

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR UTAH LIGHT DISTILLATE

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual ASTM D-86 Temp. °F
IBP	215	160
10	294	237
20	356	308
30	407	368
40	437	402
50	457	442
60	470	460
70	491	490
80	515	513
90	550	559
FBP	641	598

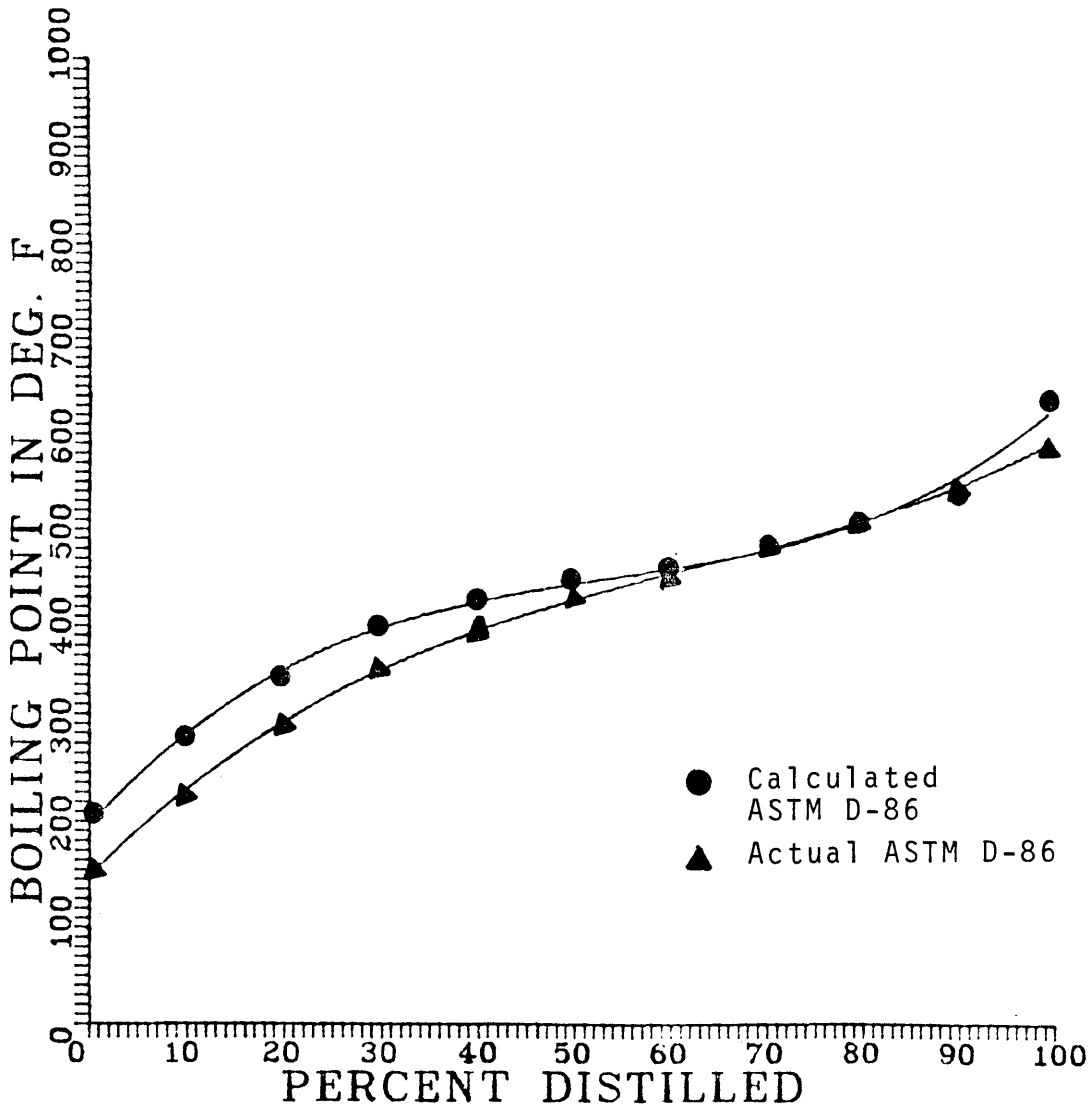

Fig. 11 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR UTAH LIGHT DISTILLATE

TABLE 14

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR WESTERN KENTUCKY LIGHT DISTILLATE

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual ASTM D-86 Temp. °F
IBP	203	170
10	281	240
20	343	292
30	390	355
40	423	402
50	456	445
60	475	480
70	509	520
80	544	550
90	589	582
FBP	602	585

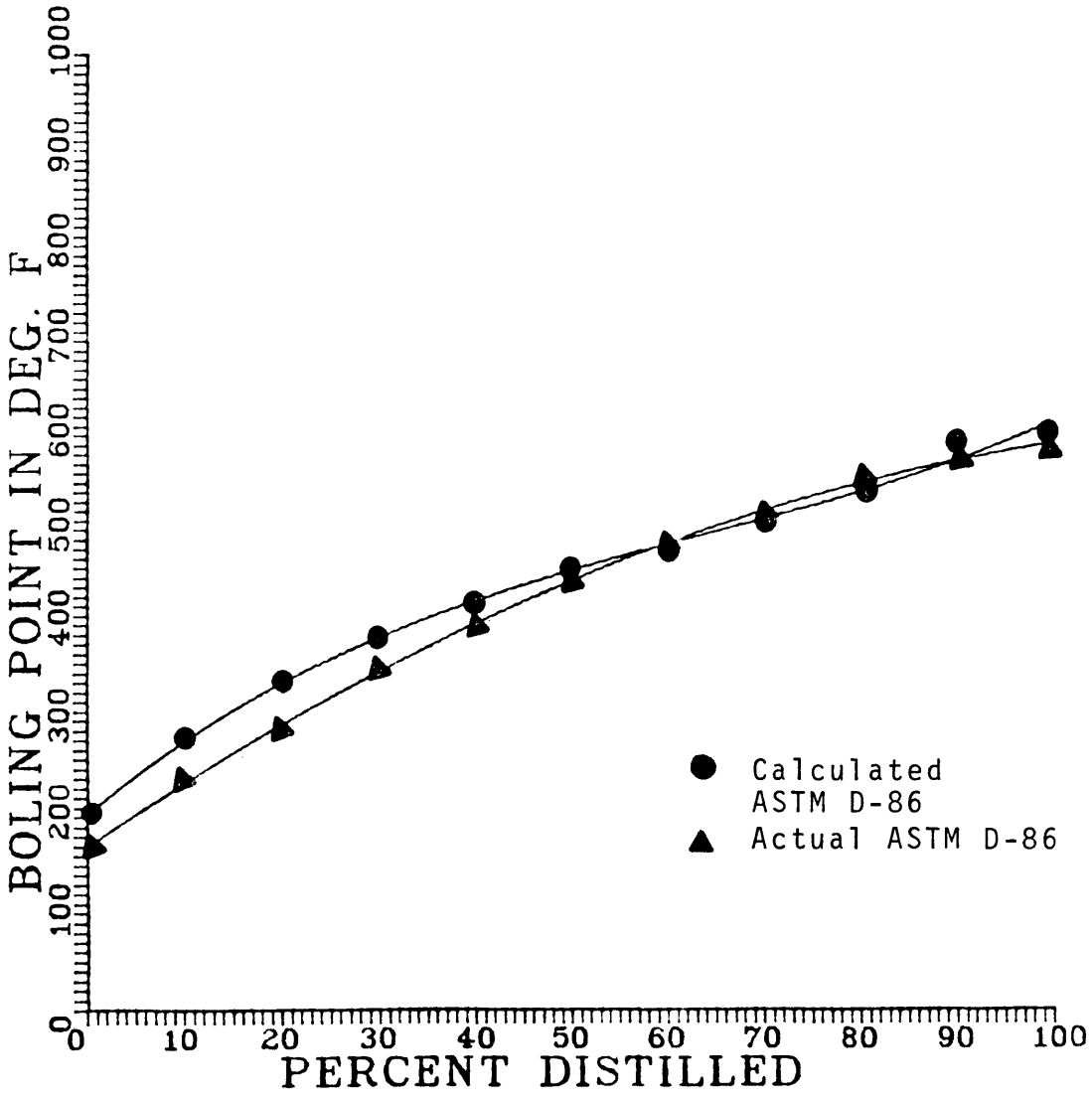

Fig. 12 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR WESTERN KENTUCKY LIGHT DISTILLATE

TABLE 15

COMPARISON OF THE CALCULATED ASTM D-86 DISTILLATION WITH THE ACTUAL ASTM D-86 DISTILLATION FOR SYNTHOIL

Percent Distilled	Calculated ASTM D-86 Temp. °F	Actual ASTM D-86 Temp. °F
IBP	297	208
10	407	420
20	432	435
30	448	450
40	462	462
50	478	480
60	500	504
70	514	525
80	530	555
90	562	605
FBP	658	635

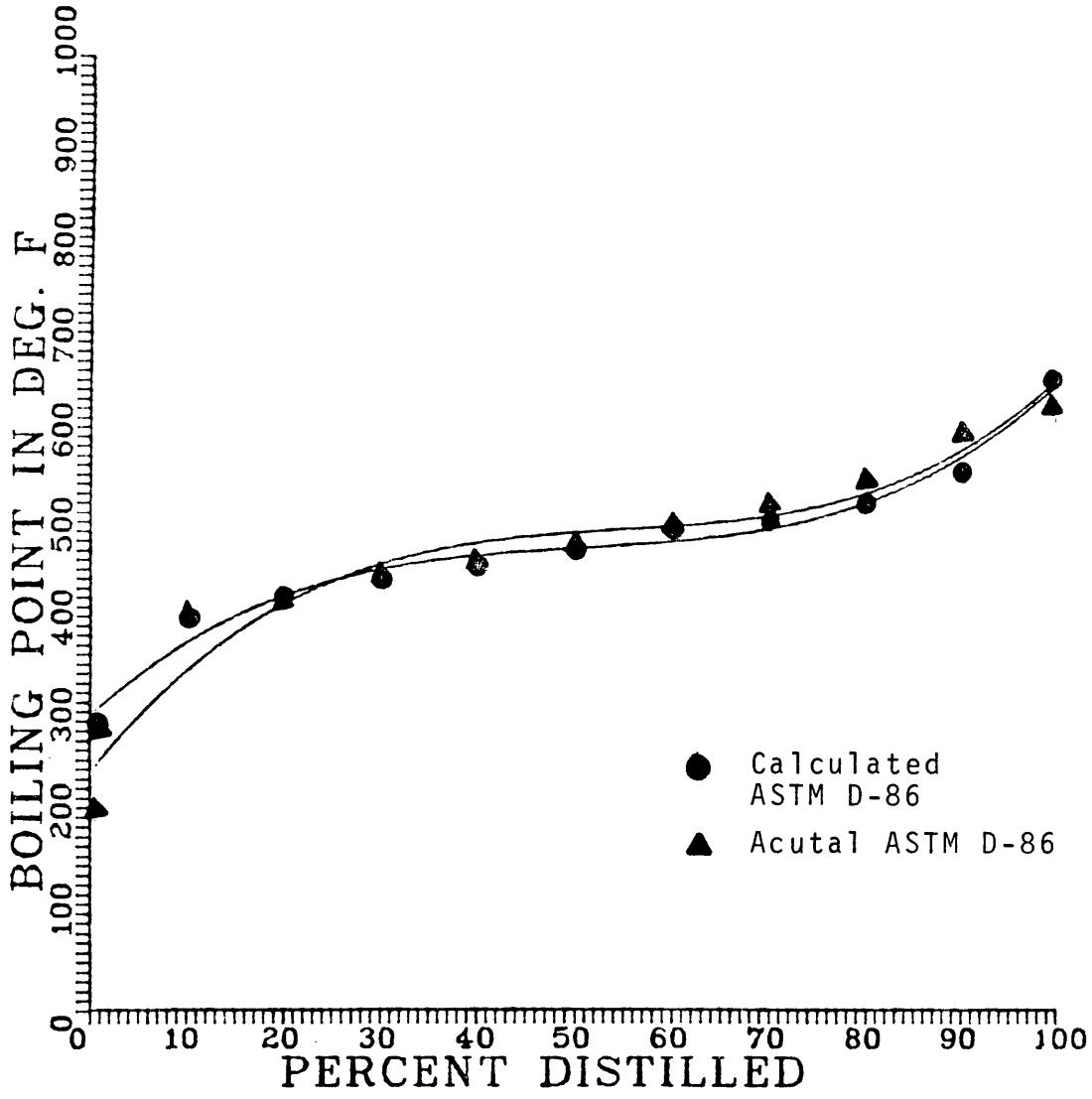

FIG. 13 COMPARISON BETWEEN THE CALCULATED ASTM D-86 AND THE ACTUAL ASTM D-86 DISTILLATIONS FOR SYNTHOIL

Results and Discussion

The simulated distillation results obtained on the various coal-derived liquid samples are compiled in the tables and figures of Appendix A. When these results are converted to the ASTM D-86 distillation, they do not show a meaningful relationship when compared to the actual ASTM D-86 distillation. This is very surprising, since many laboratories use this method successfully even-though their calibration was based on a homologous series of normal paraffins. The suspected sources of this behavior are: first, the Standard ASTM D-2887 method is usually carried out on wider boiling range samples which may not be applicable over middle boiling range samples such as 1046 Naphtha and SRC-I Naphtha. These samples show large deviation. In other words, the normal paraffin calibration mixture may be adequate up to a certain temperature range; perhaps a lower temperature range requires calibration with typical compounds derived from coal.

Second, the API correlation used to convert the TBP data into ASTM D-86 distillation data might cause severe error because it is mainly developed for petroleum fractions but not for coal-derived liquids which are significantly more aromatic and have much greater hetero-atomic contents than conventional petroleum fractions.

Therefore, it is essential to develop new correlations that could be applied for such coal-derived liquids.

Third, the high polar heteroatomic content of the samples and asphaltenes in some samples can quickly foul the chromatograph column yielding retention times out of calibration. The successful use of the gas-liquid chromatograph for simulated distillation on coal-derived liquids is dependent upon frequent regeneration of the chromatographic column and daily calibration, in addition to optimization of operating conditions.

Coal-derived liquids are complex mixtures that contain so many hydrocarbons. Many investigators did hydrocarbon-type analyses using mass spectrometry and high performance liquid chromatography on these coal-derived liquids that were produced by different processes (21,22). The hydrocarbon types were found to be saturates, olefins, aromatics (polar and non-polar), and asphaltenes. These studies show that synthoil which is produced by the synthoil process is mostly aromatic, whereas western Kentucky and Utah coal liquids which are produced by COED process have less aromatic contents. Differences in aromaticity for such coal-derived liquids are attributed to the severity of hydrogenation, to the different processes that produce these coal-derived liquids, and the boiling range temperature. The presence

of such aromatic compounds at a certain boiling range might cause discrepancies in the simulated distillation results because they elute at times when they shouldn't.

The effect of hetroatomic compounds and aromatic compounds in the simulated distillation of coal-derived liquids has been investigated in this study, by selecting model compounds that contain oxygen, nitrogen, sulphur and aromatic species. The model compounds chosen are: Benzene, Thiophene, Pyridine, 2-6 dimethyl pyridine, phenol, m-cresol, Quinoline, 1-methyl naphthalene, and dibenzothiophene. These compounds were injected separately into the same gas chromatographic column under identical operating conditions used for the Standard and the samples. The retention time for each model compound was recorded and the corresponding boiling point was obtained from the calibration curve (figure 2) and compared with the actual boiling point obtained from the literature. This comparison is shown in table 26. From this comparison, it is clear that the actual boiling points of pyridine, phenol, m-cresol, quinoline and dibenzothiophene do not agree with the boiling points obtained from the calibration curve. This means that the nitrogen, oxygen and sulphur compounds elute at earlier retention times than they should. For the rest of the model compounds the actual boiling point is approximately

equal to the boiling point obtained from the calibration curve. This means that they elute at the expected retention time corresponding to their actual boiling points. This behavior may be attributed to the presence of the methyl groups that are attached to the ring compounds.

Two coal-derived liquid samples, SRC-I Naphtha and 1046 Naphtha, are spiked with those model compounds to see the exact effect of the heteroaromatic compounds on coal-derived liquids. A series of gas chromatographic runs were made on these two samples. The model compounds were identified and their retention time is recorded and tabulated in Tables 27 and 28. The retention times obtained are similar to those obtained when the model compounds were injected separately. This means that the nitrogen, oxygen, and sulphur contents in the coal-derived liquid samples can cause discrepancies on simulated distillation data because they elute so early, a fact which can cause severe errors in the true boiling point distribution data.

Summary

True boiling point distributions for eight coal-derived liquids and two petroleum liquids are reported in Appendix A. These distributions are generated using the simulated distillation procedure according to the ASTM D-2887 Method.

A normal paraffin Standard mixture was used to generate TBP distributions for all the samples under study. This Standard is reasonably accurate for the two petroleum liquids, but for coal-derived liquid samples the Standard could not provide good TBP results when converted and compared with the ASTM D-86 distillation because of the vastly different nature of coal liquids compared to petroleum liquids.

The simulated distillation method for coal-derived liquids requires an appropriate gas chromatographic column, and an accurate temperature programming system, along with an accurate correlation for converting the TBP distillation data to the ASTM D-86 distillation data.

CONCLUSIONS

The simulated distillation method used in this study is an accurate and precise technique for generating true boiling point distributions for the petroleum fractions.

The simulated distillation method can be improved by selecting a suitable standard mixture which may contain normal paraffin, aromatic, and heteroaromatic compounds. This standard mixture may lead to accurate true boiling point distribution data.

The higher heteroatomic (oxygen, nitrogen, sulphur) contents are believed to be responsible for the deviation in the true boiling point distillation data. The increase in the heteroatomic content is most likely caused by the thermal degradation of the sample which leads to the formation of other heteroatomic compounds which are eluted earlier than expected, causing errors in the TBP distillations.

RECOMMENDATIONS

1. The gas chromatographic column must be kept in a fresh condition and it should be conditioned weekly to avoid any baseline drifts and column bleeding.
2. The injection port should be cleaned every other day and the capillary tube inside the injection port should be replaced to avoid any sample deposits which might prevent other samples from reaching the column during injection.
3. The gas chromatograph must have a calibration check every day and a blank run before sample injection is recommended to get rid of any traces of the previous sample.
4. The size of the sample to be injected each run should be as minimum as possible to avoid detector saturation, a fact that might give ghost peaks.
5. The flame ionization detector jets should be cleaned weekly to avoid any silicon deposits which might clog the jets and give error in the gas flow rate.
6. The use of a more polar gas chromatographic column may improve the TBP results using the n-paraffin Standard.
7. The Joule-Thomson valve that is used for the sub-ambient system should be maintained properly to avoid its plugging which is caused by the impurities that might

come with the CO_2 gas. The use of a gas filter in the flow stream might help in preventing that from happening.

8. The use of fresh coal-derived liquid samples is necessary for this kind of research.

9. It is recommended that some other distillation techniques be performed on these coal-derived liquids beside the ASTM D-86 distillation method and that the results obtained be compared with the simulated distillation results to see how accurate the SIMDIS method is.

10. Development of a new correlation to interconvert distillation data for coal-derived liquids rather than using the API correlation, is strongly recommended.

11. More chemical and physical analysis should be directed to these coal liquids to study their nature compared to petroleum fractions, and to measure the amounts of the heteroatomic and aromatic contents at different boiling ranges.

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APPENDIX A

TABLE 16

TPB DISTRIBUTION USING SIMDIS FOR EUGENE ISLAND WELL

Retention Time Min.	Percent Distilled	Boiling Point °F
6.20	IBP	90
12.80	10	220
16.50	20	293
20.30	30	368
23.40	40	432
26.40	50	490
29.40	60	552
32.45	70	612
35.80	80	678
39.50	90	752
46.00	FBP	904

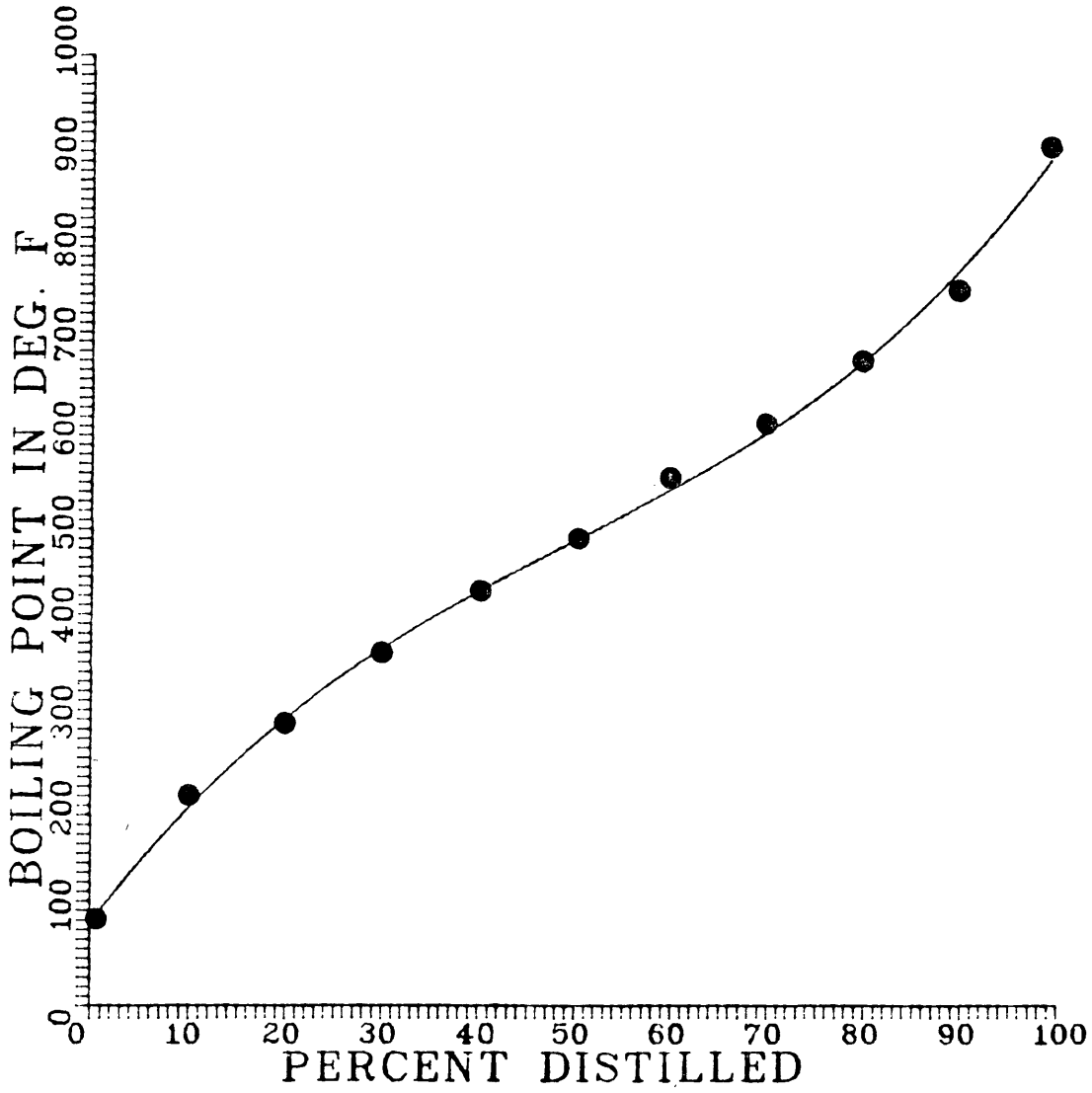


FIG. 14 SIMDIS TBP DISTRIBUTION FOR EUGENE ISLAND WELL 57/3 LIQUID #3

TABLE 17

TBP DISTRIBUTION USING SIMDIS FOR ASTM REFERENCE GAS OIL # 1

Retention Time Min.	Percent Distilled	Boiling Point °F
12.90	IBP	225
18.90	10	340
23.60	20	435
27.10	30	505
29.70	40	555
31.75	50	595
33.50	60	632
35.60	70	672
37.40	80	710
39.90	90	760
47.40	FBP	882

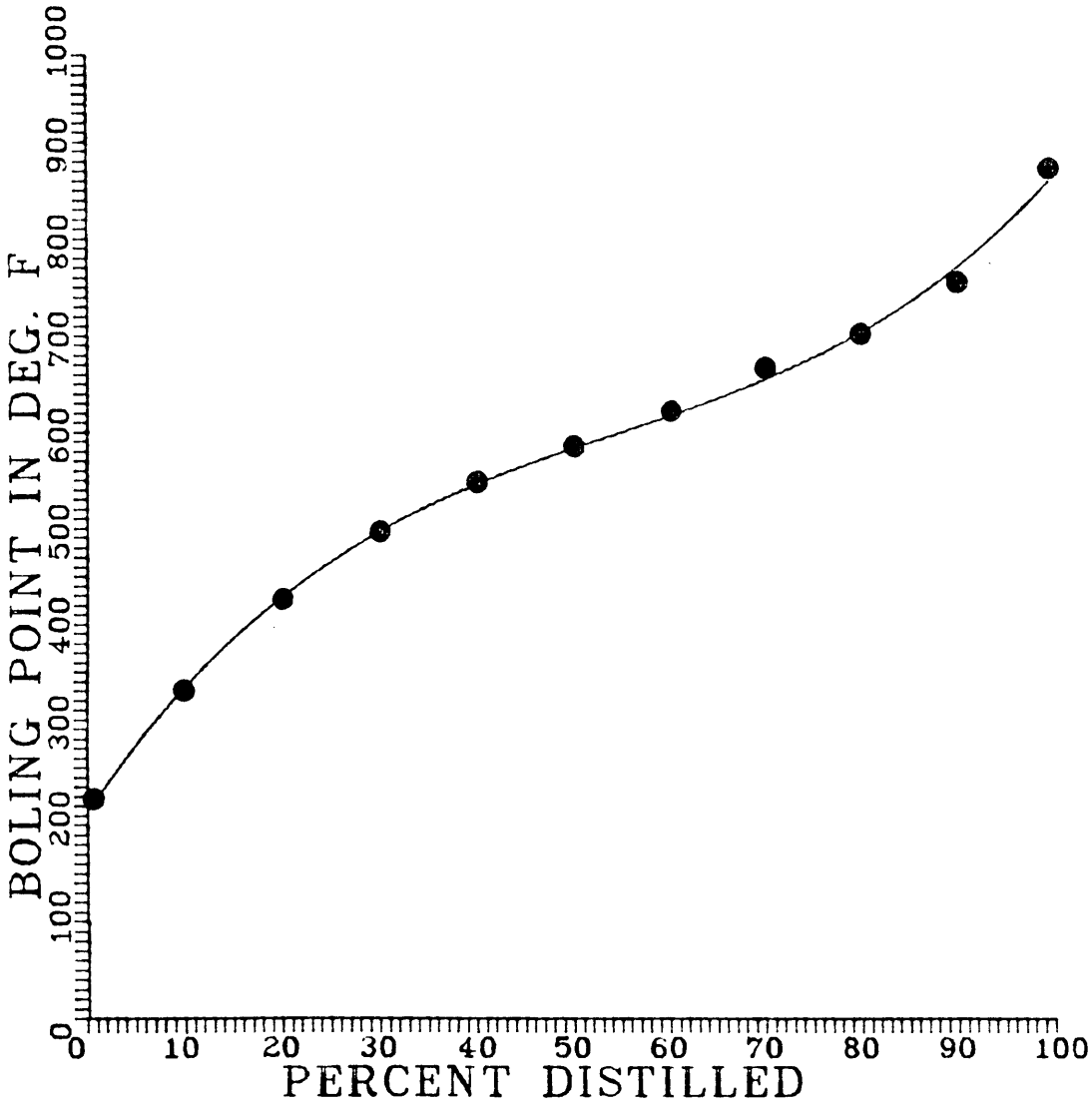


FIG. 15 SIMDIS TBP DISTRIBUTION FOR ASTM REFERENCE GAS OIL # 1

TABLE 18

TBP DISTRIBUTION USING SIMDIS FOR 1046 NAPHTHA

Retention Time, Min.	Percent Distilled	Boiling Point °F
7.12	TBP	128
10.10	10	186
11.90	20	220
13.30	30	245
14.20	40	265
14.65	50	275
16.60	60	310
17.50	70	328
18.60	80	347
20.12	90	378
21.58	95	405
22.20	FBP	470

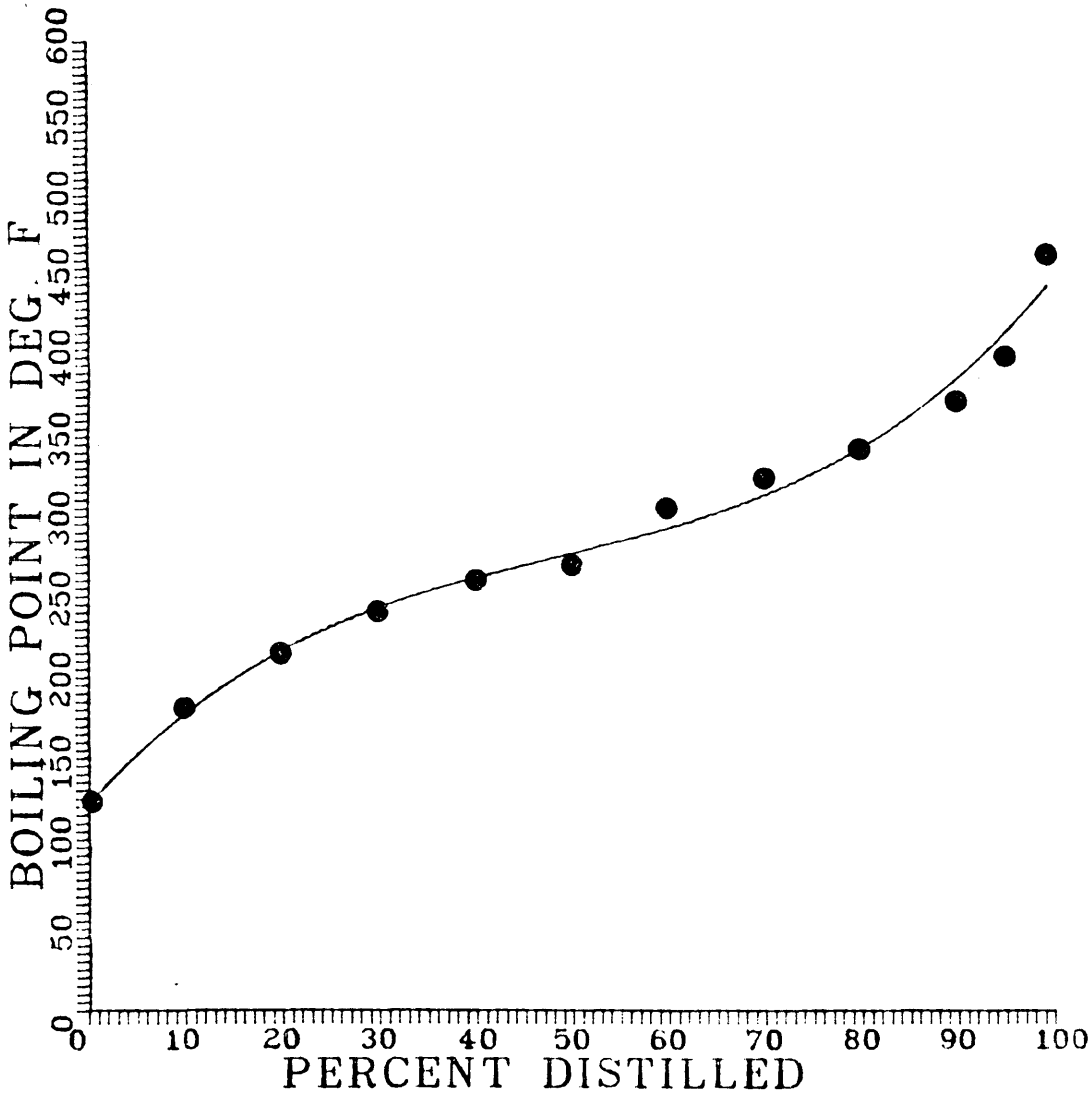


FIG. 16 SIMDIS TBP DISTRIBUTION FOR 1046 NAPHTHA

TABLE 19

TBP DISTRIBUTION USING SIMDIS FOR SRC II-500 CUT

Retention Time, Min.	Percent Distilled	Poiling Point °F
19.70	IBP	367
22.50	10	425
23.80	20	450
24.80	30	470
25.72	40	486
26.30	50	500
27.00	60	513
27.60	70	525
28.76	80	545
29.84	90	570
33.20	FBP	625

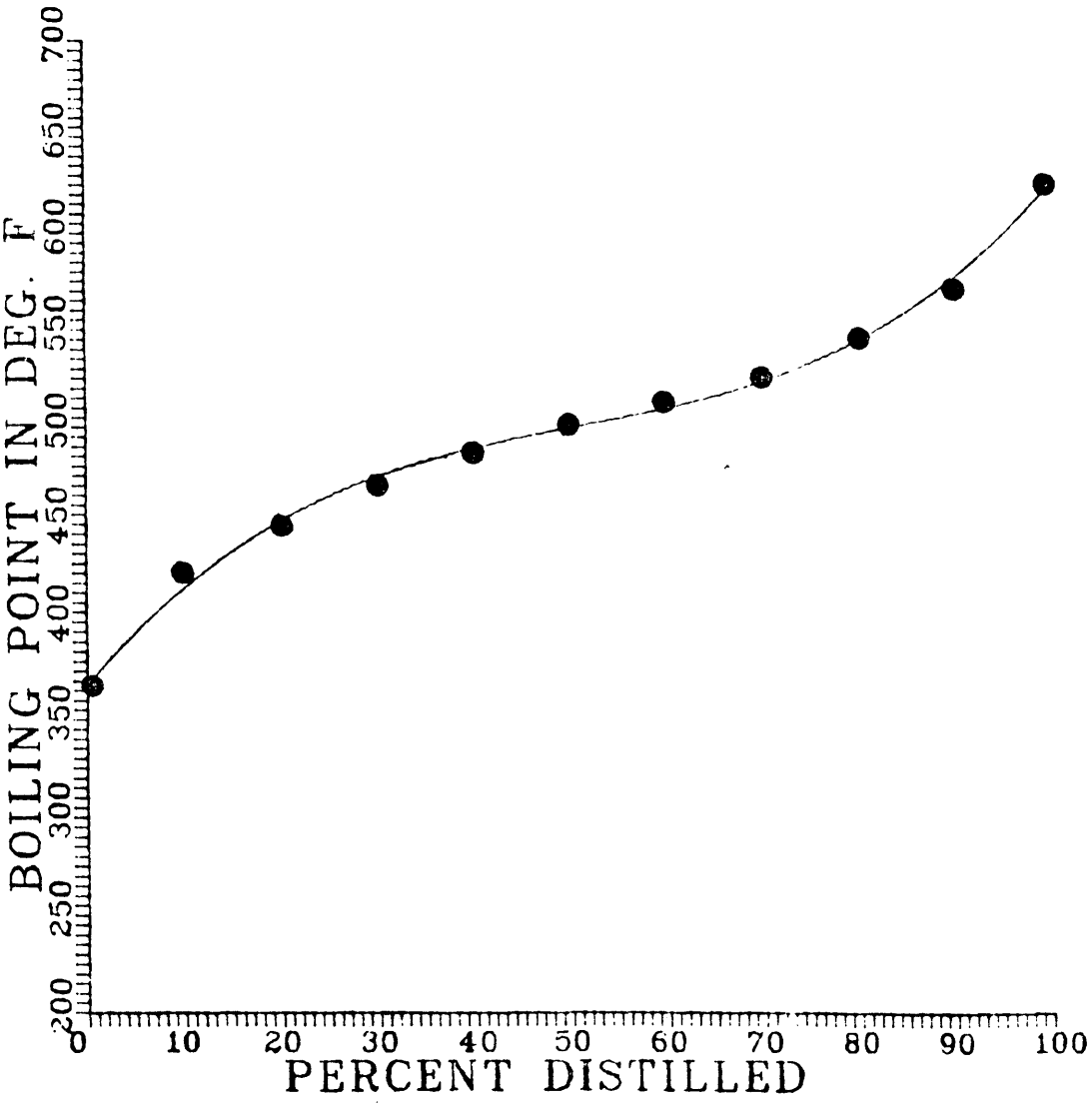


FIG. 17 SIMDIS TBP DISTRIBUTION FOR SRC II-500 CUT

TABLE 20

TBP DISTRIBUTION USING SIMDIS FOR SRC II-600 CUT

Retention Time, Min.	Percent Distilled	Boiling Point °F
25.20	FBP	485
28.00	10	548
28.65	20	568
30.00	30	580
31.00	40	596
31.32	50	605
31.60	60	612
31.95	70	618
32.50	80	628
33.62	90	648
36.45	FBP	700

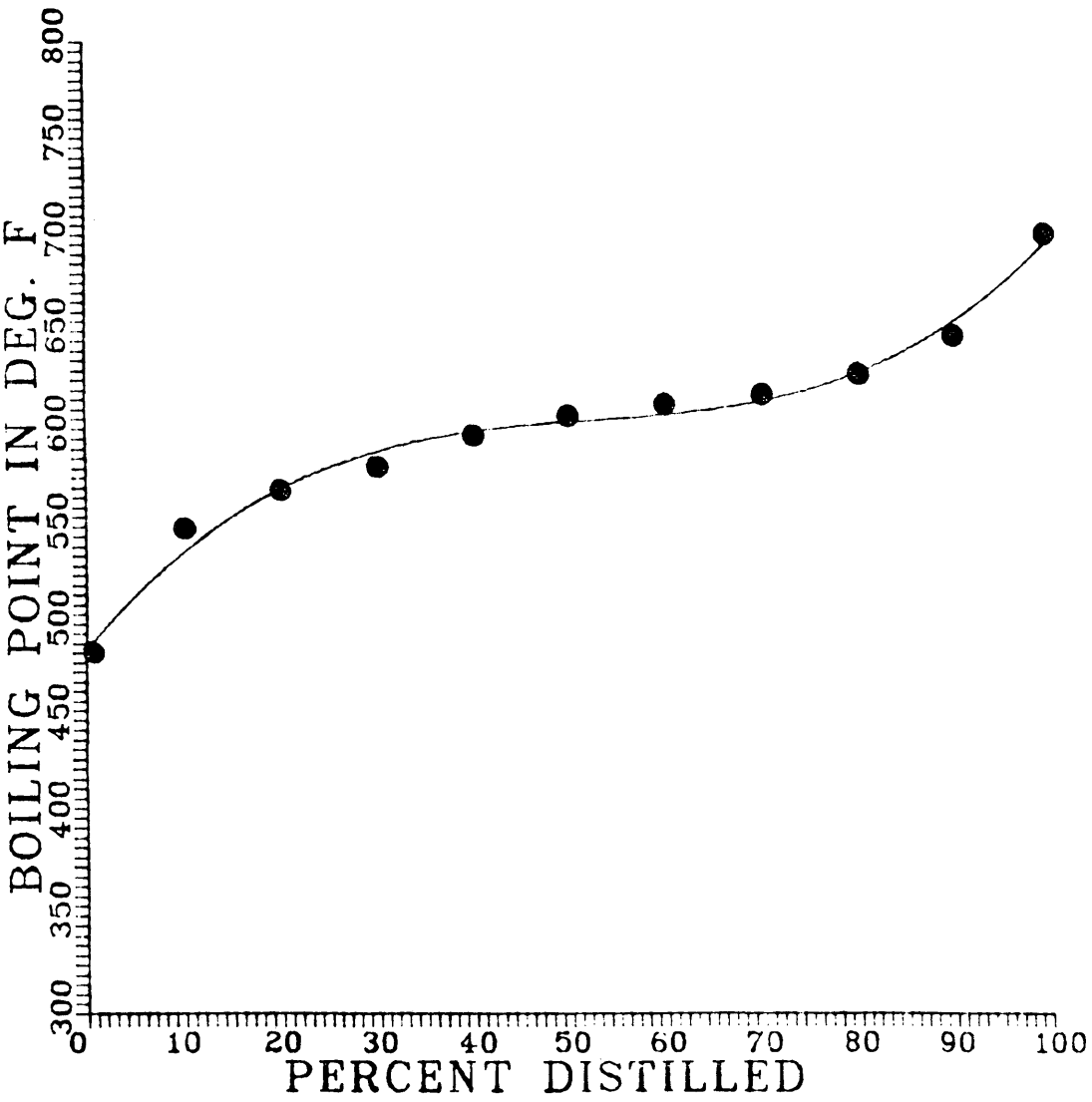


FIG. 18 SIMDIS TBP DISTRIBUTION FOR SRC II-600 CUT

TABLE 21

TBP DISTRIBUTION USING SIMDIS FOR SRC-I NAPHTHA

Retention Time, Min.	Percent Distilled	Boiling Point °F
9.10	IBP	150
11.50	10	200
12.70	20	225
13.75	30	245
14.72	40	265
15.70	50	285
16.65	60	304
17.60	70	323
18.65	80	343
20.00	90	373
24.00	FBP	455

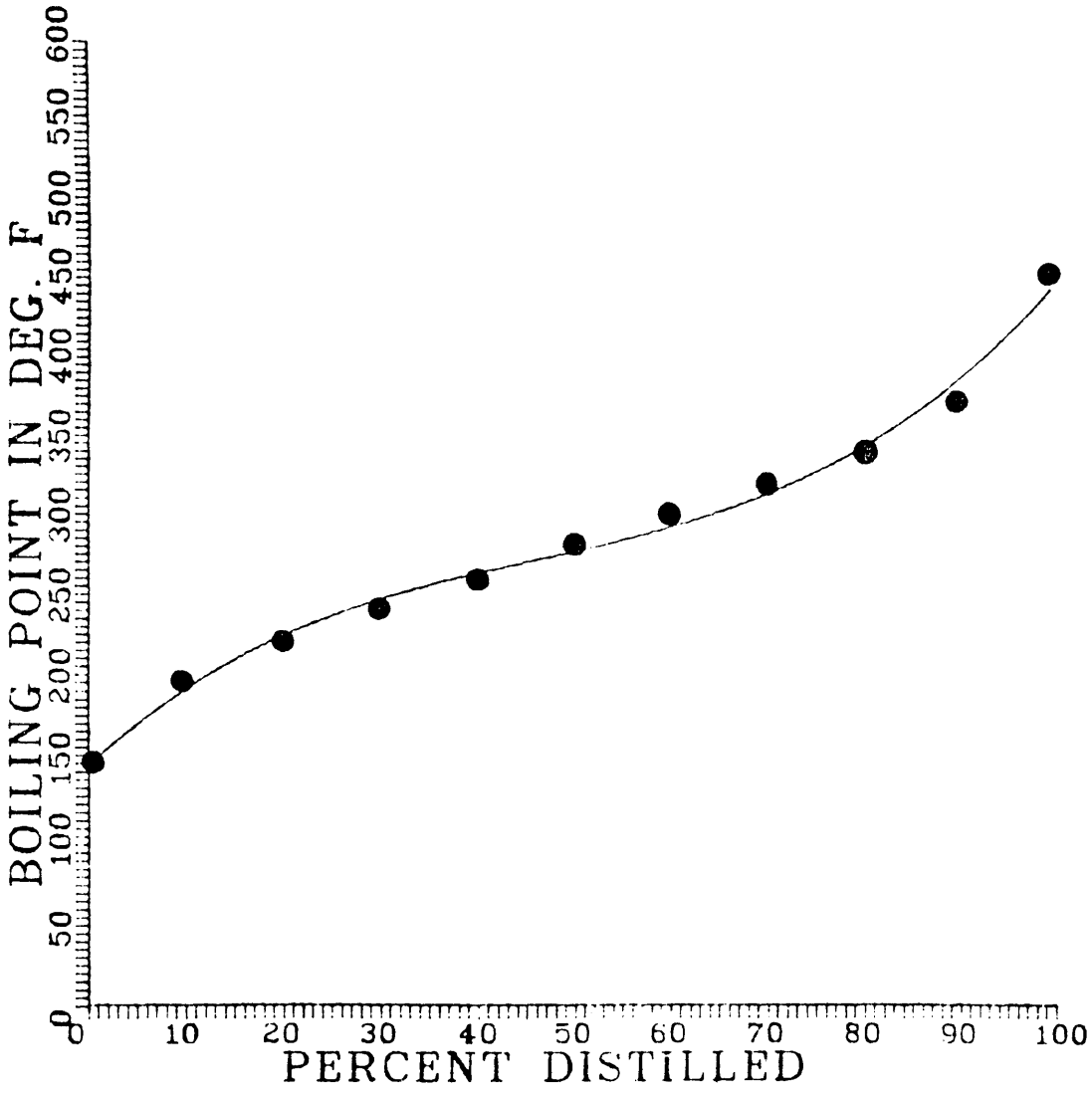


FIG. 19 SIMDIS TBP DISTRIBUTION FOR SRC-I NAPHTHA

TABLE 22

TBP DISTRIBUTION USING SIMDIS FOR "878" MIDDLE DISTILLATE

Retention Time, Min.	Percent Distilled	Boiling Point °F
15.80	IBP	295
20.30	10	380
21.50	20	405
22.00	30	415
22.80	40	430
23.70	50	450
24.64	60	467
25.60	70	490
26.80	80	510
27.60	90	525
30.30	FBP	580

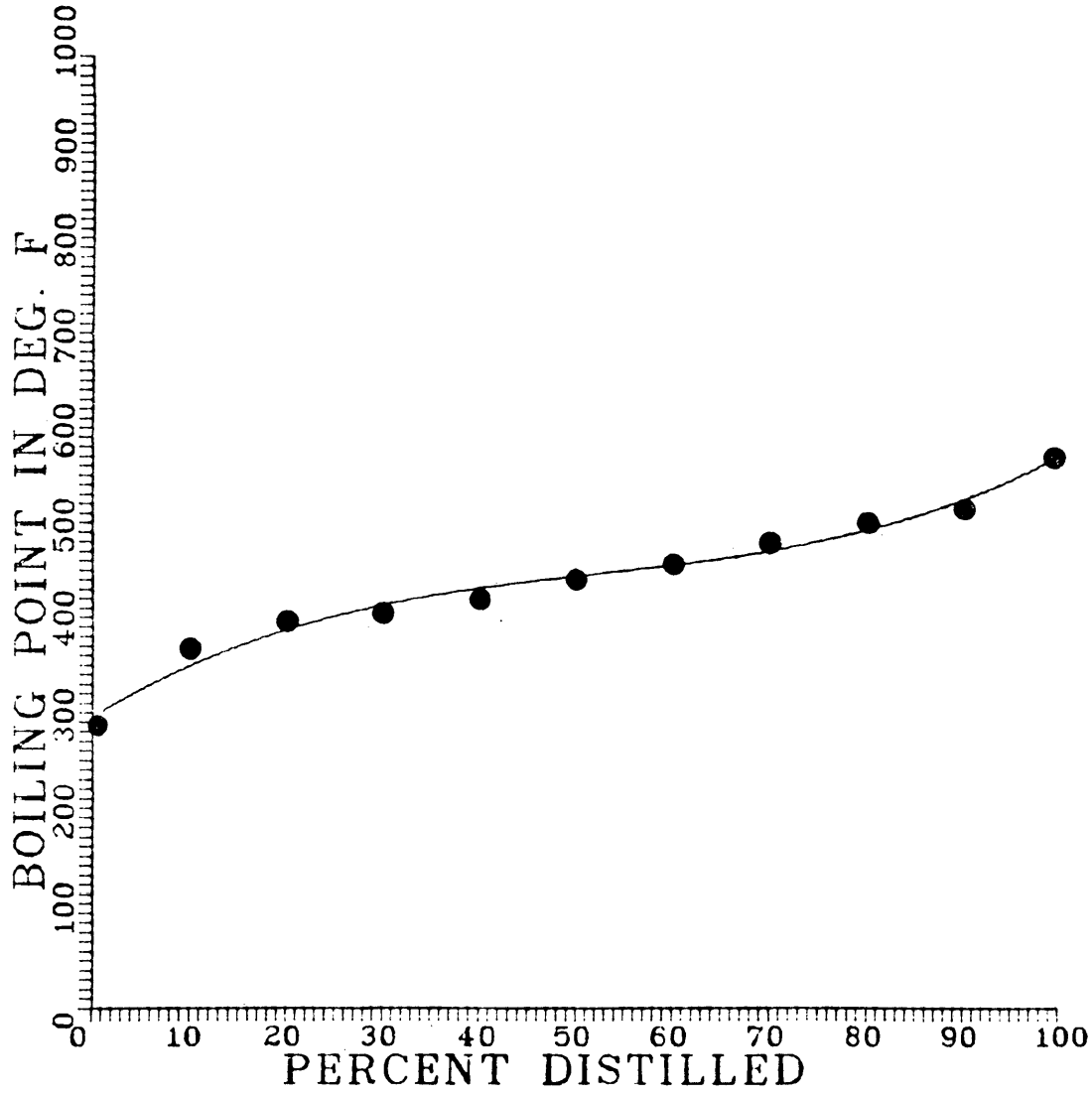


FIG. 20 SIMDIS TBP DISTRIBUTION FOR "878" MIDDLE DISTILLATE

T-2650

TABLE 23

TBP DISTRIBUTION USING SIMDIS FOR UTAH LIGHT DISTILLATE

Retention Time, Min.	Percent Distilled	Boiling Point °F
8.80	IBP	145
14.00	10	260
19.00	20	350
20.95	30	390
22.80	40	427
24.40	50	460
25.60	60	485
26.80	70	508
28.10	80	535
30.20	90	577
35.90	FBP	692

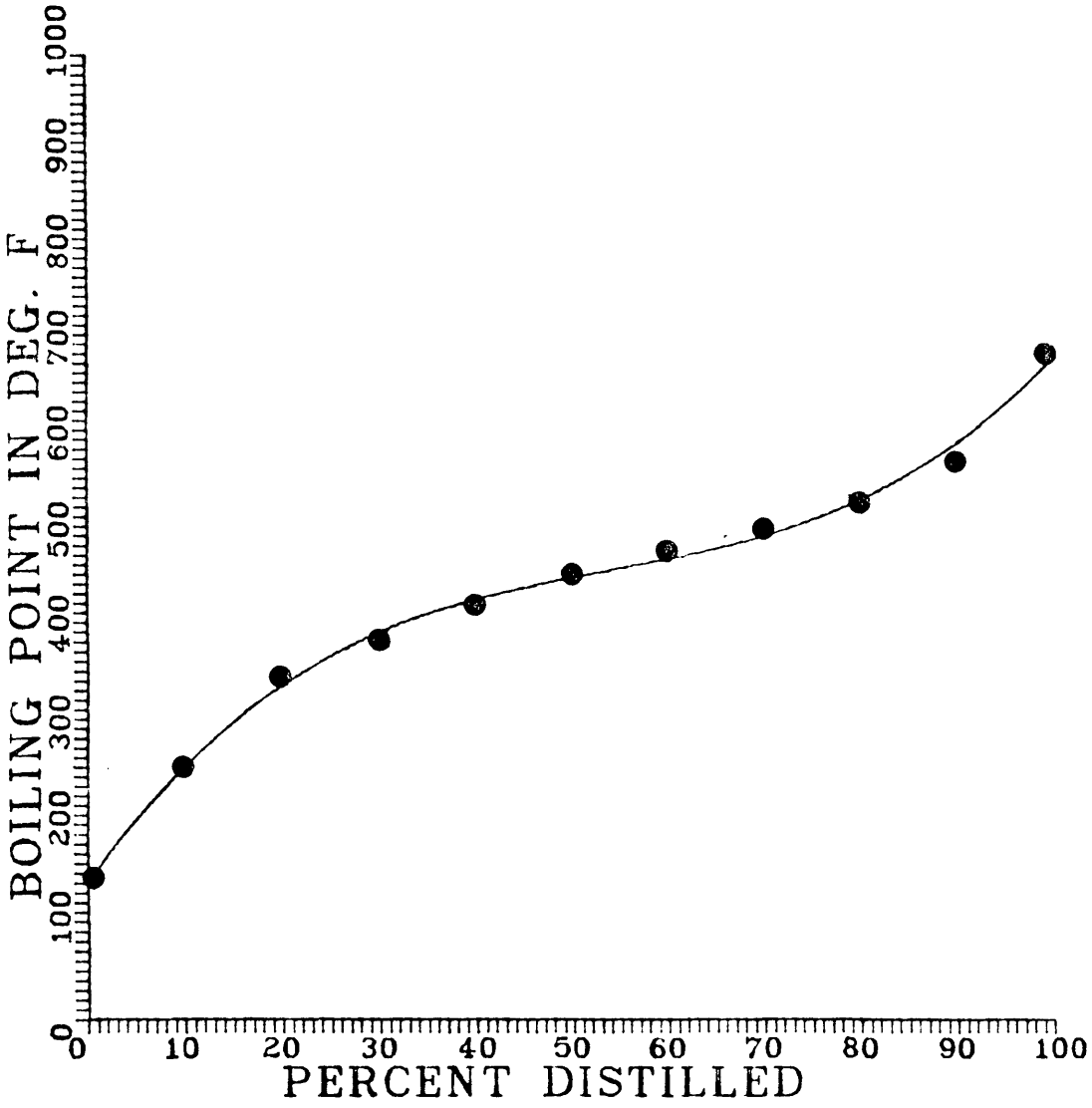


FIG.21 SIMDIS TBP DISTRIBUTION FOR UTAH LIGHT DISTILLATE

TABLE 24

TBP DISTRIBUTION USING SIMDIS FOR WESTERN KENTUCKY LIGHT DISTILLATE

Retention Time, Min.	Percent Distilled	Boiling Point °F
7.20	IBP	133
14.95	10	247
17.50	20	320
20.00	30	373
22.52	40	421
24.30	50	459
26.00	60	493
27.72	70	527
29.40	80	561
31.75	90	615
40.46	FBP	788

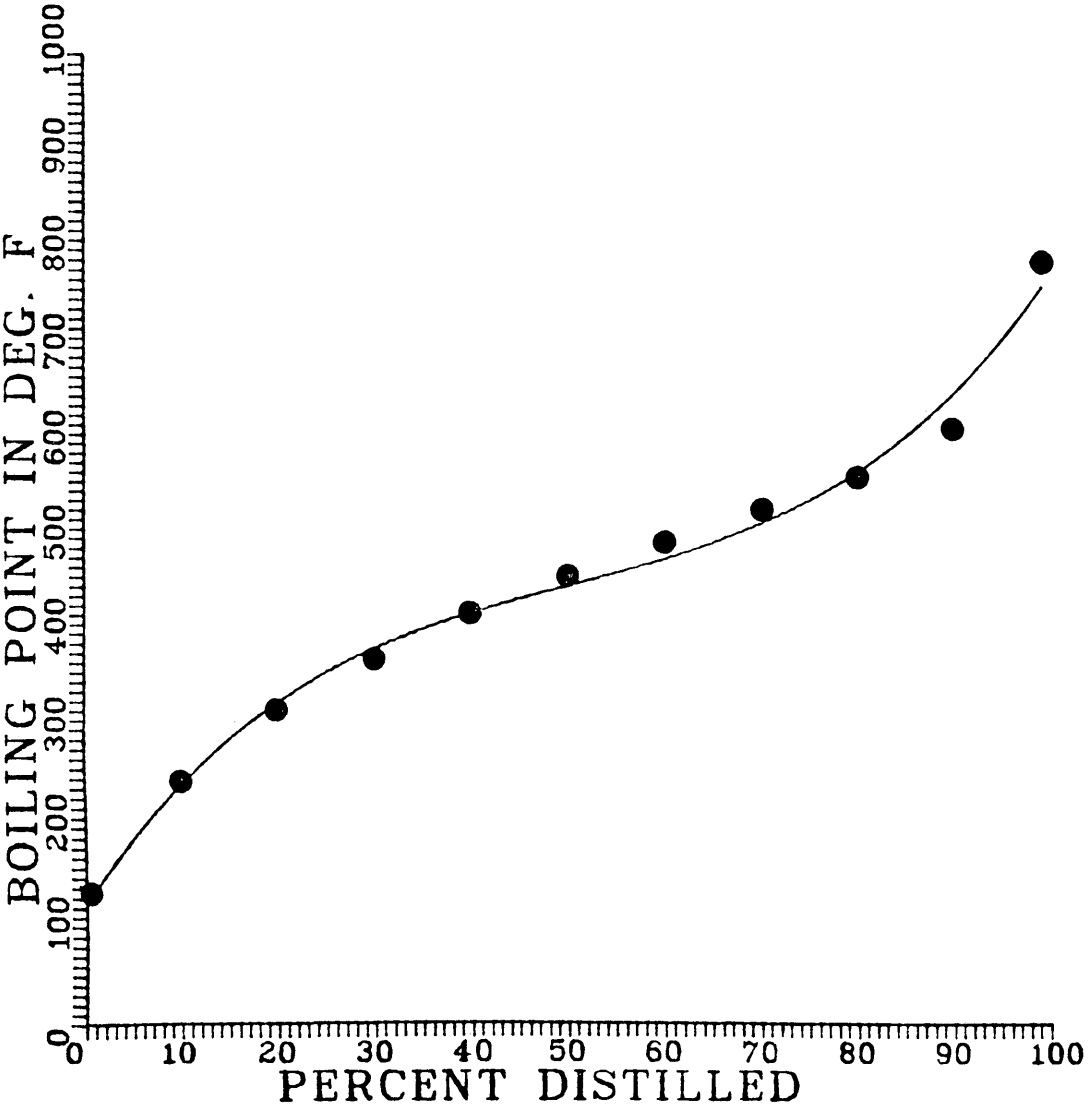


Fig. 22 SIMDIS TBP DISTRIBUTION FOR WESTERN KENTUCKY LIGHT DISTILLATE

TABLE 25

TBP DISTRIBUTION USING SIMDIS FOR SYNTHOIL

Retention Time, Min.	Percent Distilled	Boiling Point °F
12.00	IBP	210
19.80	10	366
21.60	20	405
23.00	30	432
24.20	40	456
25.35	50	480
26.50	60	502
27.85	70	530
29.00	80	554
31.20	90	598
37.50	FBP	725

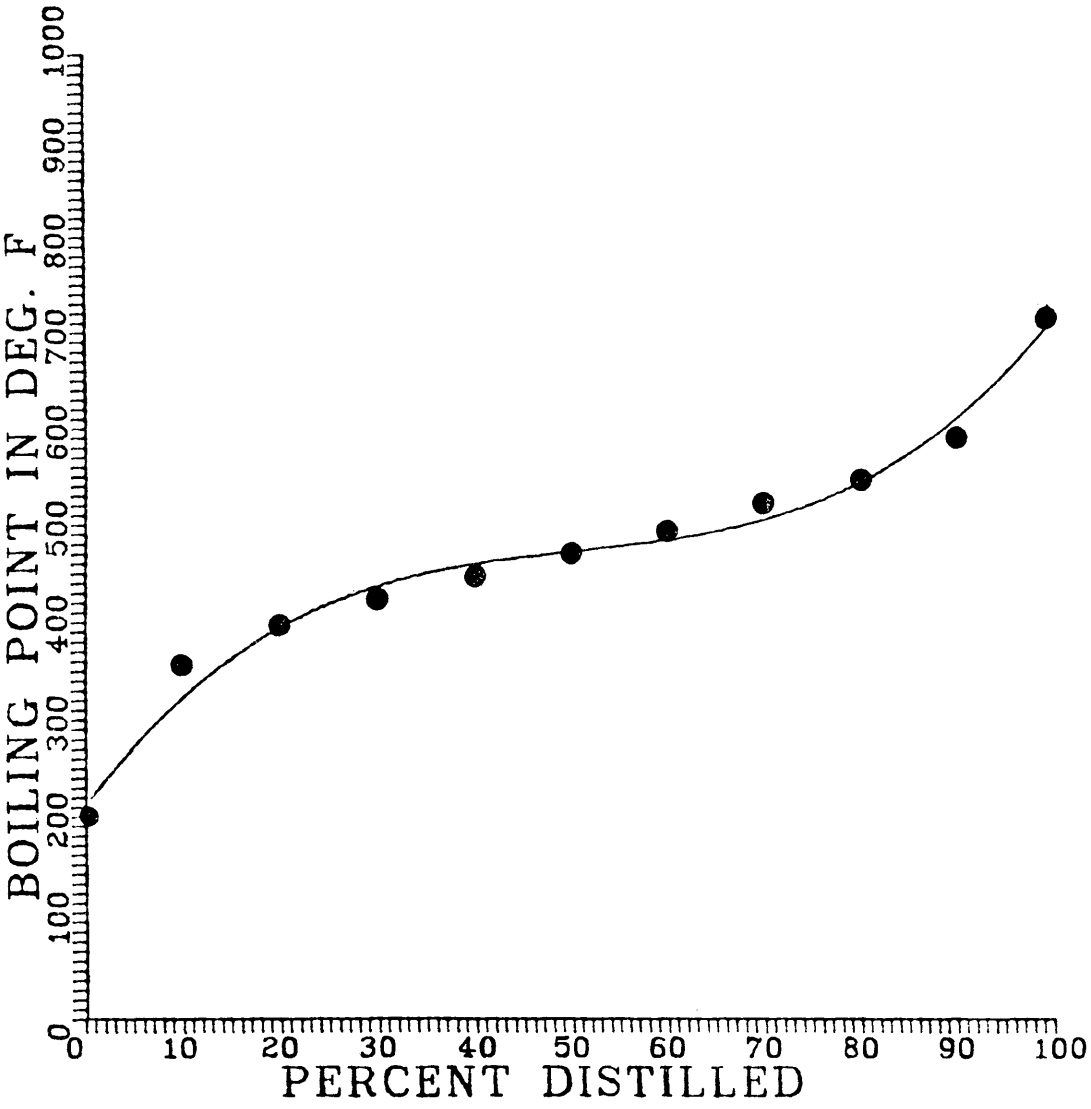
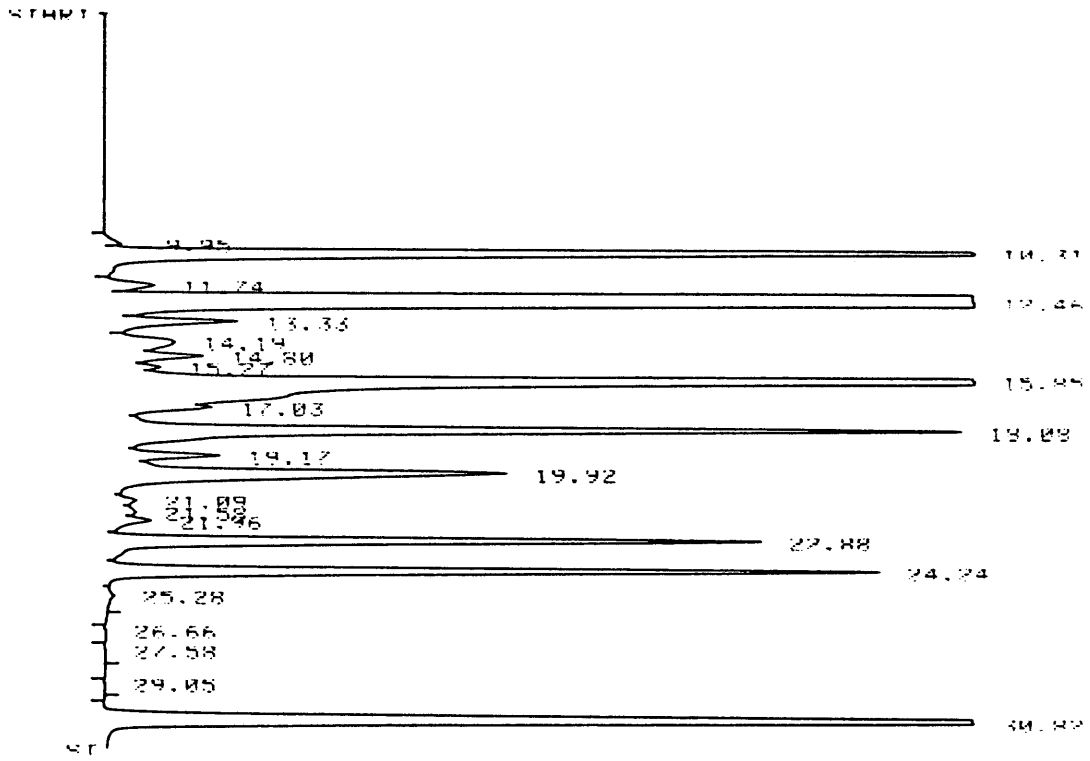


FIG. 23 SIMDIS TBP DISTRIBUTION FOR SYNTHOIL

APPENDIX B



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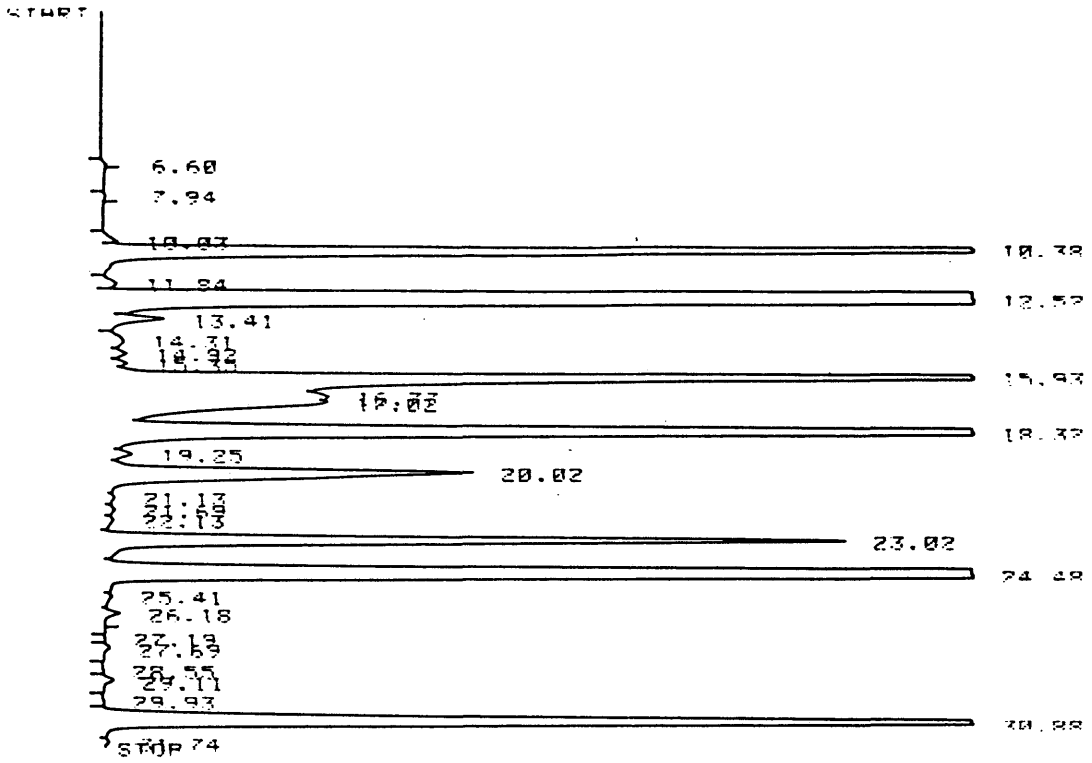
13.33	50220	1.129
14.19	43610	0.980
14.80	37870	0.851
15.27	17080	0.384
15.85	742200	16.682
17.03	38550	0.866
19.00	348200	7.826
19.17	43860	0.986
19.92	206900	4.650
21.09	12830	0.288
21.58	13960	0.314
21.96	20900	0.470
22.88	228400	5.131
24.24	255600	5.745
30.82	451100	10.139

AREA THRESH: 1.0000 E+ 0

FIG. 24 GC RUN REPRESENTING THE NINE MODEL COMPOUNDS WHEN THEY ARE SPIKED WITH SRC I NAPHTHA



HP RUN #1163 HPR/11/82 TIME 21:27:54
ID:1
AREA %

VT	AREA	AREA %
10.48	470600	9.264
12.52	1429000	28.132
13.41	24210	0.477
14.31	12760	0.251
15.93	535800	10.548
16.77	88440	1.741
17.62	128200	2.524
18.32	587700	11.570
19.25	11260	0.222
20.02	189400	3.729
23.02	267300	5.262
24.48	892600	17.572
30.88	442400	8.709

RF FACTOR: 1.0000 E+ 0

FIG. 25 GC RUN REPRESENTING THE NINE MODEL COMPOUNDS WHEN THEY ARE SPIKED WITH 1046 NAPHTHA

TABLE 26

COMPARISON BETWEEN THE ACTUAL BOILING POINT AND THE BOILING POINT OBTAINED FROM THE CALIBRATION CURVE FOR THE SELECTED MODEL COMPOUND

Compound	Retention Time Min*	Boiling Point °F	
		Calibration	Actual
Benzene	10.17	174	176
Thiophene	10.46	181	183
Pyridine	12.68	225	240
2-6,dimethyl pyridine	15.88	290	291
Phenol	18.57	347	358
M-cresol	20.15	377	397
Quinoline	23.24	442	459
1-methyl napthalene	24.54	468	472
Dibenzo thiophene	31.12	600	614

*The retention time is the average of at least three separate runs

TABLE 27 RETENTION TIMES OF THE MODEL COMPOUNDS IN THE 1046 NAPHTHA

Sample Name - 1046 Naphtha

RETENTION TIME IN MINUTES

Mixture	Benzene	m-cresol	Quinoline	Thiophene	1-m-naphtha-lene	2-6 dimethyl pyridine	Phenol	Pyridine	Thiophene
S+B	10.14	-	-	-	-	-	-	-	-
S+B+m-cr	10.12	20.09	-	-	-	-	-	-	-
S+B+m-cr+Q	10.11	20.11	23.02	-	-	-	-	-	-
S+B+m-cr+Q+T	10.34	19.86	22.85	10.34	-	-	-	-	-
S+B+m-cr+Q+T+1-m-Nap	10.27	20.15	23.09	10.27	24.47	-	-	-	-
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm Py	10.26	20.08	23.00	10.26	24.33	15.90	-	-	-
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm-Py + Ph	10.25	20.02	23.06	10.25	24.50	15.81	18.45		
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm-Py+Ph+Py	10.30	19.95	22.94	10.30	24.39	15.84	18.23	12.43	-
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm-Py+Ph+Py+Dib.T	10.35	19.99	22.98	10.35	24.44	15.89	18.31	12.48	30.88

S: Sample
B: Benzene
m-cr: m-cresol
Q: Quinoline
1-m-nap: 1-methyl naphthalene
2-6 dm-Py: 2-6,dimethyl pryidine
Ph: Phenol
Py: Pyridine
Dib.T: Dibenzothiophene
T: Thiophene

TABLE 28 RETENTION TIMES OF THE MODEL COMPOUNDS IN THE SRC I NAPHTHA

Sample Name - SRC I Naphtha

RETENTION TIME IN MINUTES

Mixture	Benzene	m-cresol	Quinoline	Thiophene	1-m-naphtha-lene	2-6 dimethyl pyridine	Phenol	Pyridine	Thiophene
S+B	10.11	-	-	-	-	-	-	-	-
S+B+m-cr	9.98	19.88	-	-	-	-	-	-	-
S+B+m-cr+Q	10.18	20.13	22.89	-	-	-	-	-	-
S+B+m-cr+Q+T	10.24	20.17	22.92	10.24	-	-	-	-	-
S+B+m-cr+Q+T+1-m-Nap	10.19	19.96	22.83	10.19	24.33	-	-	-	-
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm Py	10.18	19.97	22.80	10.18	24.05	15.80	-	-	-
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm Py+Ph	10.18	19.90	22.81	10.18	24.12	15.77	18.08	-	
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm Py+Ph+Py	10.31	19.92	22.88	10.31	24.24	15.84	18.09	12.47	
S+B+m-cr+Q+T+1-m-Nap+ 2-6 dm Py+Ph+Py+Dib T	10.31	19.92	22.88	10.31	24.24	15.85	10.08	12.46	30.82

S: Sample
B: Benzene
m-cr: M-cresol
Q: Quinoline
1-m-Nap: 1-methyl naphthalene
2-6 dm-Py: 2-6,dimethyl pyridine
Ph: Phenol
Py: Pyridine
Dib.T: Dibenzothiophene
T: Thiophene

APPENDIX C

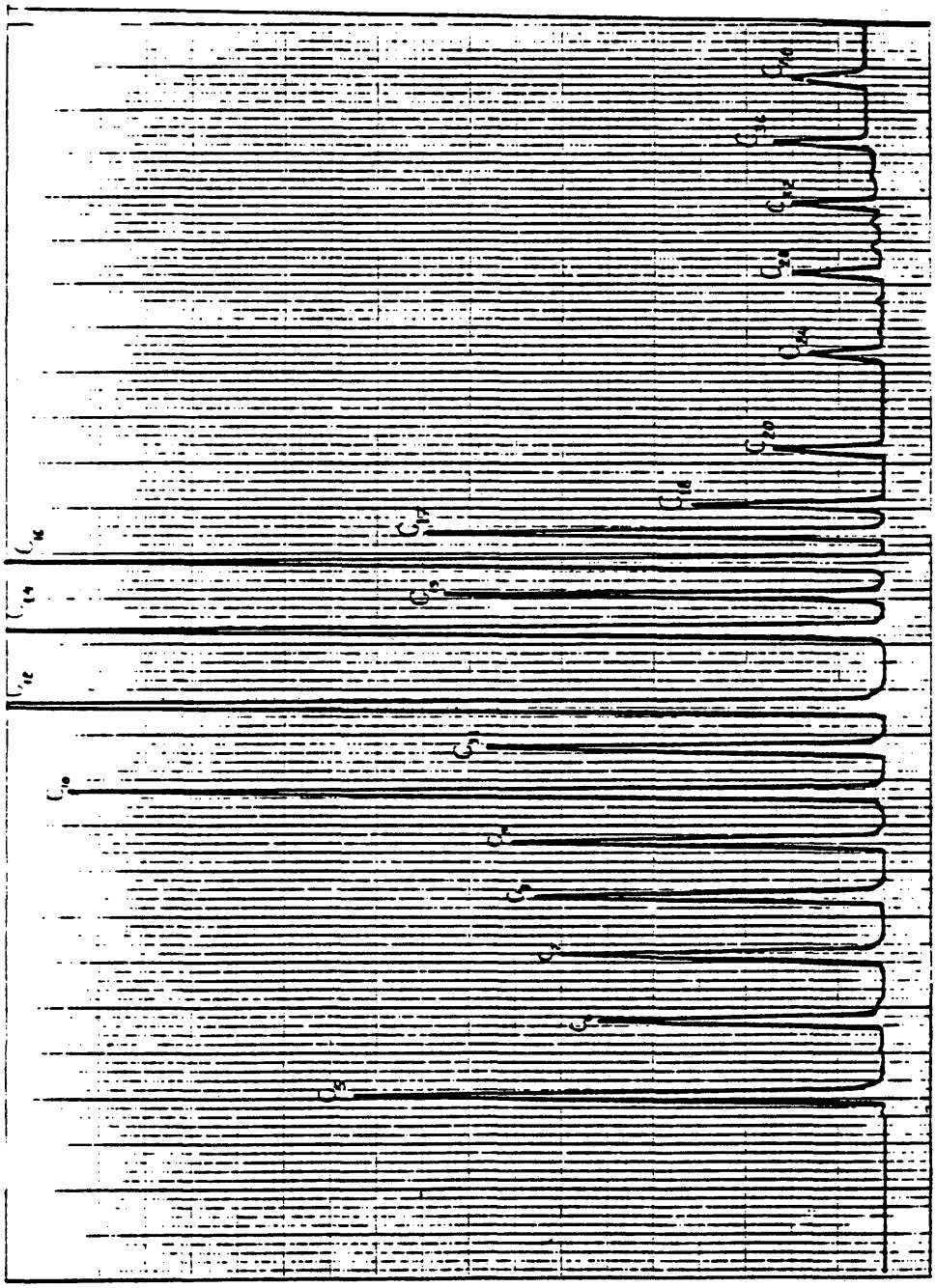
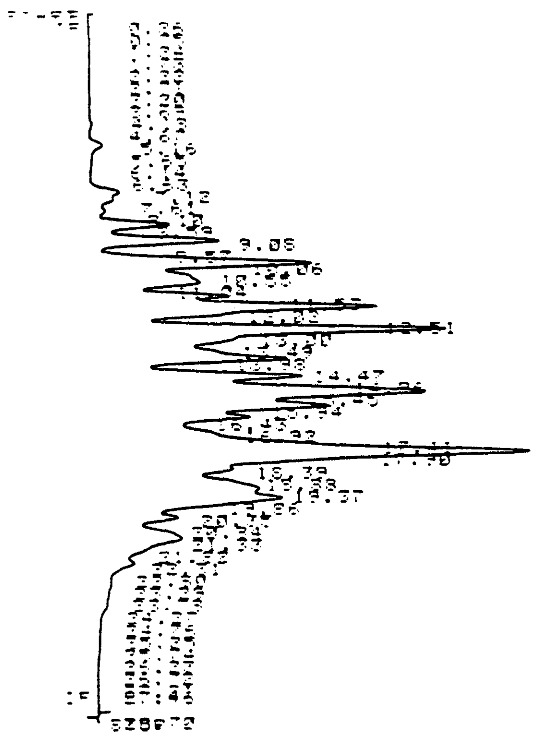


FIG.26 CHROMATOGRAM FOR THE NORMAL PARAFFIN STANDARD MIXTURE



RUN # 351 MAR 01 88

AREA %

RT	AREA	AREA %
4.13	3642	0.018
4.67	4362	0.024
5.16	33960	0.164
5.65	19990	0.097
6.14	6720	0.032
6.47	7651	0.019
7.17	95840	0.464
7.61	98100	0.475
8.10	65460	0.317
8.59	267700	1.296
9.05	359500	1.742
9.57	179700	0.870
10.04	783900	3.795
10.55	473400	2.292
11.04	439600	2.129
11.57	589300	2.853
12.[illegible]	1060000	5.132
13.51	564700	2.734
[illegible]	1260000	6.100
13.49	609200	2.949
[illegible]	792000	3.834
14.47	499200	2.416
14.9[illegible]	903200	4.373
[illegible]	1419000	6.870
[illegible]	1029000	4.982
16.37	693800	3.359
16.[illegible]	537500	2.593
17.41	909200	4.402
17.87	1870000	9.859
18.39	853800	4.133
18.89	632900	3.063
19.77	816600	3.953
19.[illegible]	813200	3.936
20.75	405700	1.964
20.[illegible]	304800	1.476
21.33	416500	2.016
21.27	267400	1.295
21.31	186500	0.907
22.80	107100	0.518
23.39	82300	0.398
23.[illegible]	65260	0.316
24.[illegible]	48740	0.236
24.[illegible]	28720	0.139
25.[illegible]	24770	0.120
25.[illegible]	22180	0.107
26.23	15650	0.076
26.72	17910	0.087
27.21	14000	0.068
27.46	8099	0.039

FACTOR: 1.0000 E+ 0

FIG. 27 GC RUN REPRESENTING 1046 NAPHTHA

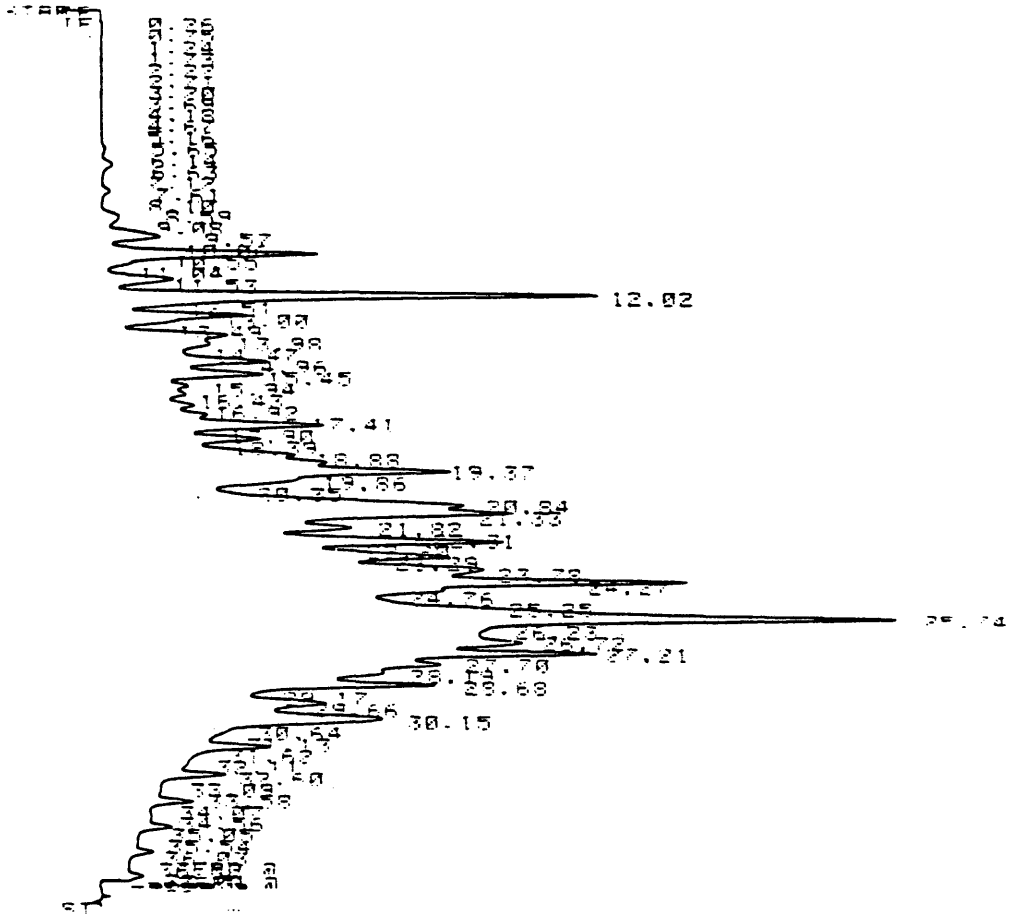


FIG. 28 GC RUN REPRESENTING
UTAH LIGHT DISTILLATE

AREA %

RT	AREA	AREA %
3.20	870	0.004
5.65	2572	0.012
6.14	4889	0.022
6.63	17250	0.079
7.12	2523	0.012
7.61	9450	0.043
8.10	3166	0.014
8.59	12920	0.059
9.08	29790	0.136
9.57	50820	0.370
10.06	58200	0.269
10.55	287300	1.315
11.04	41730	0.191
11.53	102200	0.468
12.02	323300	1.479
12.51	422300	1.932
13.00	183800	0.841
13.49	110300	0.505
13.98	224600	1.028
14.47	200600	0.918
14.96	267300	1.223
15.45	260900	1.194
15.94	183300	0.839
16.43	166200	0.761
16.92	174500	0.798
17.41	234400	1.073
17.90	332200	1.520
18.39	271000	1.240
18.88	334400	1.530
19.37	484900	2.219
19.86	548600	2.510
20.35	298200	1.365
20.84	473300	2.166
21.33	789000	3.610
21.82	507300	2.321
22.31	474400	2.171
22.80	657800	3.010
23.29	640000	2.929
23.78	714000	3.267
24.27	957200	4.380
24.76	719000	3.290
25.25	639800	2.928
25.74	1173000	5.367
26.24	1077000	4.928
26.72	814400	3.727
27.21	845000	3.867
27.70	807800	3.696
28.19	641800	2.937
28.68	566700	2.593
29.17	422400	1.933
29.66	417000	1.908
30.15	467300	2.138
30.64	398100	1.822
31.13	242400	1.109
31.62	283900	1.299
32.11	188800	0.864
32.60	206900	0.947
33.09	143900	0.658
33.58	126900	0.581
34.07	144100	0.659
34.56	105100	0.481
35.05	119500	0.547
35.54	77340	0.354
36.03	89840	0.411
36.52	58360	0.267
37.01	72300	0.331
37.50	56480	0.258
37.99	60730	0.278

.01 FACTOR: 1.0000 E+ 0