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I. CONTRACT OBJECTIVE

The objective of the contract is to develop a catalyst and operating conditions for the direct conversion of syngas to liquid hydrocarbon fuels, using microporous crystals ("Molecular Sieves") in combination with transition metals.

## II. SCHEDULE

The contract work was planned for the 36-month period beginning March 6, 1981.

Work on the program is divided into four tasks.

Task 1, essentially completed, was the conversion of low molecular weight liquids, such as methanol and propylene, to gasoline and diesel fuel, with catalysts consisting of only a Molecular-Sieve component, commonly designated as the shape-selective component (SSC).

Task 2 is the conversion of syngas (carbon monoxide and hydrogen) to gasoline and diesel fuel, using catalysts consisting of both an SSC and a transition-metal component (MC).

Task 3 is a study of the surface effects and reaction intermediates present on various catalysts during the hydrogenation of carbon monoxide. This task is conducted under a subcontract with the University of California at Berkeley, and is directed by Dr. Gabor A. Somorjai.

Task 4 comprises the management and technical reports for the contract.

III. ORGANIZATION

Synthesizing "Liquid Hydrocarbon Fuels from Syngas" is the goal of a research and development program on catalysis conducted by the Molecular Sieve Department, Catalysts and Process Systems Division, Union Carbide Corporation.

The work is performed at Union Carbide Corporation's Tarrytown Technical Center, Tarrytown NY 10591.

Principal investigator is Dr. Jule A. Rabo.

Program manager is Dr. Albert C. Frost.

#### IV. SUMMARY OF PROGRESS

##### A. Task 1

Task 1 has been essentially completed. Only minimal work, if any, is contemplated in future.

##### B. Task 2

For the 11 catalysts reported for February through April 1983, the metal components were either potassium-promoted iron, cobalt, or thorium-promoted cobalt. The shape-selective components were various Molecular Sieves. In two of these, the two components were combined in their dry states as a simple physical mixture. In all others the components were combined by precipitating the metal oxide from an aqueous slurry of the Molecular Sieve.

The method of promoting each catalyst depended on how it was made.

With each of the two catalysts made as a simple physical mixture, the metal component was promoted alone, before it was mixed with the Molecular Sieve component. The others, made by precipitation of the metal component in the slurried Molecular Sieve, were promoted by impregnation of the combined product.

For a detailed description of these methods, see Appendixes A and B. For details of the test results, see Appendix B.

### Iron Component Test Results

The five iron catalysts reported in this quarter were all promoted with potassium. Two of them were the physically mixed catalysts; in these, the Molecular-Sieve components were UCC-109 and UCC-111. The three others were precipitate-slurry catalysts with LZ-105-6, UCC-104 and UCC-107 as their Molecular-Sieve components.

The most promising results were obtained with the catalyst containing UCC-111 (Appendix B, Run 10225-3). In earlier studies UCC-111 alone had been found to be a poor Task 1 catalyst for oligomerizing propylene. Physically combined with potassium-promoted iron, however, it proved surprisingly effective as a syngas catalyst in Task 2. It produced straight-chain olefinic hydrocarbons, as a normal Fischer-Tropsch catalyst does, but unlike the normal Fischer-Tropsch catalyst, it may also have isomerized the carbon-carbon double bond. Transfer of the double bond from the usual Position 1, typical for Fischer-Tropsch products, to an interior position, should not only lower the pour point of the liquid product, but it should raise its octane number as well. For instance, 1-octene has a blending RON of 25 while those of 3- and 4-octene are 95 and 99, respectively.

Another effective catalyst was the one containing LZ-105-6, which yielded steady conversions and product distributions (Appendix B, Run 10225-1). Although isomerization of pentane decreased at first, the quantity of isomerate in the product cuts remained high. Its gasoline yield and apparent quality of pro-

duct, were comparable to those of the physically-mixed iron/potassium and UCC-104 catalyst (Second Annual Report, Run 10011-10). Its total fuels (gasoline plus diesel) appear, however, to be lower than that of the UCC-104 catalyst.

The catalyst containing UCC-109 also yielded steady conversions and product distributions (Appendix B, Run 10011-17). However, the quantity of isomerate in the product cuts decreased rapidly, suggesting that the highly acidic UCC-109 component was probably coking.

The catalyst containing UCC-104, prepared during this quarter by precipitation of iron oxide in a UCC-104 slurry, was found to have negligible activity (Appendix B, Run 10225-4). So also was the catalyst containing UCC-107, prepared in the same way (Appendix B, Run 10112-11).

The low activity of the UCC-104 catalyst is in marked contrast to the high activity found for its physically-mixed form (Second Annual Report, Run 10011-10). This finding, as well as the generally high activities of the LZ-105-6 catalyst described above (Appendix B, Run 10225-1) and the cobalt catalysts described below (including one containing UCC-107); suggest that the precipitate-slurry mode of synthesis has an effect on catalytic activity which is not yet predictable.

#### Cobalt Component Test Results

Four of the six cobalt catalysts reported this quarter were promoted with either thorium or thorium and potassium. All six were synthesized by the precipitate-slurry method, with either



LZ-105-6, LZ-Y-82, UCC-101 or UCC-107 as the Molecular Sieve component. The test results for most of these catalysts indicate that cobalt is more effective than iron in producing a high yield of motor fuels. For instance, the cobalt catalysts containing LZ-105, LZ-Y-82, UCC-101 and UCC-107 produced motor fuel yields in the range of 68 to 73 percent (Appendix B, Runs 10112-6, 10112-10, 10112-4 and 10625-2, respectively).

This increase in motor fuel yield was due primarily to a higher yield of diesel oil, with the gasoline yield remaining approximately the same as for the iron catalysts. This increased diesel oil yield, as well as an increased methane yield, was balanced against a decreased C<sub>2</sub>-C<sub>4</sub> yield. The yields of the heavy fractions for both metal catalysts remained relatively low.

With all the cobalt catalysts there was a gradual deactivation of both their conversions and the acid activities of their Molecular Sieve components. Loss of acid activity was reflected by liquid products with a continually decreasing degree of isomerization and an attendant increasing degree of waxing.

The loss of acid activity of the catalyst containing LZ-Y-82 (Appendix B, Run 10112-10) was somewhat more gradual than anticipated from the Task 1 studies. In Task 1, LZ-Y-82 deactivated more quickly than UCC-109 (Second Annual Report, Runs 9972-19 and 10112-1) which, in turn, deactivated quickly with iron/potassium as its metal component (Appendix B, Run 10011-7). Lowering of the LZ-Y-82 deactivation rate may have been caused by the lowering of its initial activity from a partial ion exchange of its

acid sites by the impregnated potassium.

Such redistribution of the impregnated promoter within the catalyst matrix may also explain the insignificant differences between the product distributions (a primary function of the metal component) of the cobalt and UCC-101 catalyst (Appendix B, Run 10112-4) and the cobalt/thorium and UCC-101 catalyst (Appendix B, Run 10112-7).

#### Analytical Development

Efforts to develop a routine, reliable method of analyzing hydrocarbon groupings for the total liquid products have centered on liquid chromatography techniques which were believed to be more reliable than the inaccurate FIA analysis. It is now evident that current liquid chromatographic technology is not capable of making these determinations (Appendix C).

#### C. Task 3

Studies at the University of California at Berkeley, under the direction of Professor G. A. Somorjai, have concentrated on the investigation of thorium oxide and new rhodium catalysts. Thorium oxide was found to be an active catalyst for synthesizing methanol, and unlike catalysts based on copper oxide it does not require carbon dioxide to maintain its activity (Appendix D).

V. CHANGES

There were no contract changes during the ninth quarter.

VI. FUTURE WORK

Efforts during the next quarter will be directed at examining the cobalt catalysts at various thorium levels, with various metal additives, and with various other Molecular Sieves.

A handwritten signature in black ink, appearing to read "A. G. Frost", written over a horizontal line.

A. G. Frost

APPENDIXES

Appendix A. CATALYST SYNTHESIS

By P. K. Coughlin

The synthesis of Task 2 catalysts during this quarter has followed two parallel paths, one based on iron as the metal component, one based on cobalt.

Trials of physical mixtures of an iron component with a Molecular Sieve were extended to include new Molecular Sieves, since this method of evaluating new Sieves for use in F-T catalysts is the easiest to interpret. The promoted iron component has a high and well-known activity for both the F-T synthesis and the water-gas shift reactions. With the aid of data previously reported, the effects of the Molecular Sieve can easily be separated from those of the iron.

A number of iron catalysts were also prepared by precipitating the iron onto the Molecular Sieve, an arrangement which sharply increases the Sieve's effect on the activity of the metal component. The Molecular Sieve has metal-support and possible particle-size effects on the metal component. Furthermore, since the Sieve affects the partition of potassium between the metal component and the Sieve, the potassium used to promote the iron is also added to the Sieve, which can impair the Sieve's acid activity. These diverse side effects rule out precipitation as the formulation of choice for evaluating a new Molecular Sieve

with iron metal. Physical-mixture catalysts not only are free of such complications, but also allow observation of the Sieve's effect on the components of the product distribution. Precipitation catalysts may, however, be useful in two ways: First, in observing a more intimate interaction of the two components, and second, whenever there are corresponding physical-mixture catalysts for comparison, in isolating and observing the side effects.

Cobalt catalysts were first reported in the Seventh Quarterly Report. Although they present difficult problems of product quality, their high selectivity for gasoline and diesel oil has been very encouraging; recently, therefore, we have given them more attention than iron catalysts. Formulation of cobalt catalysts, originally done by pore-filling alumina-bonded extrudates, has since been expanded, as with iron, to include using the techniques of precipitation and physical mixing. Cobalt catalysts are generally promoted with thorium instead of potassium.

Cobalt functions differently from iron in at least two ways. First, under the same processing conditions it is more active in Fisher-Tropsch synthesis. Second, its product, being much more paraffinic, is more difficult for the Molecular Sieve to upgrade. These differences have led to differences in formulation. Iron catalysts generally have equal weights of MC and SSC. Cobalt catalysts with the same ratio are very active, but their Molecular Sieves have little effect on the product. Cobalt catalysts with 20 percent cobalt, which are as active as 50-percent iron

catalysts, allow a 4:1 ratio of SSC to MC. Because the proportion of Molecular Sieve is much larger, its effect on the final product is correspondingly greater. The small quantity of metal component, however, requires the use of a binder to maintain the mechanical strength of the pellets formed by physical mixing. All such catalysts were formed as 15-percent silica-bonded extrudates.

Table A-1 lists the catalysts for which results are reported in Appendix B.



Table A-1. Catalysts tested this quarter.

Fe/K + UCC-109	A 50:50 physical mixture of 1% potassium-impregnated precipitated $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and UCC-109. UCC-109 is a large-pore Union Carbide proprietary Molecular Sieve. Formed as a 15% silica-bonded extrudate.
Fe/K + UCC-111	Physical mixture as above with UCC-111 instead of UCC-109. Formed as tablets with no binder.
Fe/K on LZ-105-6	$\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ was precipitated onto LZ-105-6 powder from a slurry of the zeolite in aqueous ferric nitrate to give 20% on the Sieve. The metal-loaded Molecular Sieve was then impregnated with $\text{K}_2\text{CO}_3$ solution to give 1% $\text{K}_2\text{O}$ . Formed into extrudates with 15% silica binder.
Fe/K on UCC-104	Prepared like the catalyst above but with UCC-104 (a new Union Carbide proprietary Molecular Sieve with medium pores) instead of LZ-105-6. Formed as tablets without binder.
Fe/K on UCC-107	UCC-107, a Union Carbide proprietary Molecular Sieve, was metal loaded and formed in the same manner as UCC-104.
Co on LZ-105-6	$\text{CoO}$ was precipitated onto LZ-105-6 from an aqueous $\text{CoNO}_3$ slurry of the Molecular Sieve powder by the addition of $\text{Na}_2\text{CO}_3$ . Formed as tablets without binder.
Co/Th/K on LZ-Y-82	Co was precipitated onto LZ-Y-82 by the same method used for the catalyst above. The metal-loaded powder was impregnated with a solution of $\text{K}_2\text{NO}_3$ and $\text{Th}(\text{NO}_3)_4$ to add 1% of each promoter. Air calcined two hours at 500C in Run 10112-9, at 250C in Run 1-10112-10.
Co on UCC-101	Prepared by the same method used for Co on LZ-105-6. UCC-101 is a Union Carbide proprietary Molecular Sieve of moderate acidity.
Co/Th on UCC-101	The previous catalyst was impregnated with $\text{Th}(\text{NO}_3)_4$ solution, then formed into tablets. This catalyst contained 1% Th.
Co/Th on UCC-107	Prepared by same procedure as the catalyst above except with UCC-107 instead of UCC-101.

Appendix B. CATALYST TESTING

By P. K. Coughlin, C. L. Yang, G. N. Long and L. F. Elek

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## I. INTRODUCTION

Both Bertly reactors were used exclusively for Task 2 testing this quarter.

Results of 11 tests, conducted February through April, 1983, are reported. The order in which they are reported is not chronological, but in a sequence designed to clarify each test's significance. Catalysts containing iron are reported first, followed by those containing cobalt. Within each group the tests are reported in a sequence designed to relate the results of one experiment to those of another. Actual data are presented in the same format as in previous reports.

Each catalyst designated as having a metal component "on" a Molecular Sieve was formulated by precipitating the metal component in a slurry of the Molecular Sieve powder. The metal component is predominantly on the surface of the Molecular Sieve crystallites. When such a catalyst is promoted, the metal-coated Molecular-Sieve crystallites are impregnated with the promoter, an action which affects both the metal component and the Molecular Sieve component.

Each catalyst designated as having a metal component "+" a Molecular Sieve was formulated by physically mixing the metal component with the Molecular Sieve crystallites. The metal com-

ponent is impregnated with the promotor before mixing. In this formulation the promoter affects only the metal component, not the Molecular Sieve.

II. RUN 10011-17, Fe/K + UCC-109

This catalyst had to be formulated differently from other physical mixtures reported previously, which were made by pressing the well mixed metal component and Molecular Sieve powder into tablets. Tablets made in this way with  $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ , however, had almost no physical strength, presumably because the inherently cohesive particles of  $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$  were separated to some degree by the relatively uncohesive crystallites of Molecular Sieve. Since the particles of UCC-109 are even smaller than those of  $\text{Fe}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ , and thus even more likely than standard-sized zeolite particles to surround and separate the iron particles, the Fe/K + UCC-109 mixture is exceptionally poor in pellet strength. Consequently it was extruded with a 15 weight-percent silica binder.

During the binding process the potassium promoter may possibly have migrated from the iron to the Molecular Sieve, which would lower both the promotion effect of the potassium on the iron and the acid activity of the Sieve. Analysis of the test results indicates that this alkali transfer was not significant. A major effect of potassium ion on iron is to introduce water gas shift (WGS) activity into the catalyst. The  $\text{H}_2:\text{CO}$  usage, and  $\text{CO}_2:(\text{CO}_2 + \text{H}_2\text{O})$  effluent ratios, show that the WGS activity of this catalyst is comparable to those of other physical-mixture catalysts, but much higher than those of promoted precipitation

catalysts such as that used in Run 10011-11 (Second Annual Report) where the potassium transfer to the Molecular Sieve was significant. Also, this catalyst had high initial acid activity, another sign of little alkali transfer.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C<sub>4</sub>'s, plotted against time on stream, are presented in Figs. 1-4. Simulated distillations of the entire pentane+ product of three representative samples are presented in Figs. 5-7. The carbon number product distributions of the samples are presented in Figs. 8-14. Chromatograms from the simulated distillation of the condensed products of particular samples are reproduced in Figs. 15-21. Detailed material balances are presented in Tables 1A-1C.

The syngas conversion shows only slight deactivation with time on stream (Fig. 1). After an initial loss of activity the catalyst shows very steady conversion. The carbon monoxide and hydrogen conversions are similar, showing that the WGS activity is sufficient for this catalyst to use the 1:1 hydrogen:carbon monoxide feed efficiently. For most of the test it was actually converting a 0.95:1.0 hydrogen:carbon monoxide feed. This activity is mostly a function of the metal component, and gives little indication of the stability or activity of the Molecular Sieve.

Product selectivity is also fairly constant (Fig. 2). The only reliable trend is an initial decrease in methane yield with a concomitant increase in C<sub>5</sub><sup>+</sup> yield. The methane yield of 12 weight percent is similar to that of other physically mixed cata-

lysts under comparable test conditions. Yields of gasoline and diesel oil are similar to those of the catalyst mixture containing UCC-104 (Run 10011-10), while the catalyst mixture containing Fe/K with UCC-101 (Run 10011-9) produced more diesel oil relative to gasoline. The carbon-number product distributions also imply that the operation of the catalyst was fairly steady (Figs. 8-14). The first sample (10011-17-02, Fig. 15) seems to show a double behavior, changing its slope ( $\ln \alpha$ ) at C<sub>15</sub>; the other samples show a similar double behavior to varying degrees. The effect is not as great as for the reference iron catalyst (Run 10011-6), in which the carbon distribution drastically changed  $\alpha$ 's at C<sub>20</sub>. The simulated distillation plots also show a constant product from this catalyst (Figs. 5-7). Though not identical, the three distillations are closely similar.

All these data imply very steady operation for this catalyst, but closer examination of the products shows that it may not be as steady as it seems. The Molecular Sieve component deactivated rather rapidly, clearly shown by the isomerization of the pentane (Fig. 3). Initially the acidic UCC-109 isomerized the pentane to the degree that more than 70 percent of it was isopentane. This value agrees well with the equilibrium value of 76 percent at 250C. The isomerization activity decreased exponentially until only 20 percent of the pentane was isomerized; a level only slightly greater than that produced by a F-T catalyst with no Molecular Sieve. Chromatograms from the simulated distillation of the condensed product (Figs. 15-21), show a similar loss of

isomerization activity. However, the liquid product is more highly isomerized, even at the end of the run, than the products of a normal F-T catalyst, as can be seen by comparing Figs. 15-21 with Fig. 22, the chromatogram from the reference iron catalyst (Run 10011-6).

The probable reason for the loss of acid activity is coking of the Molecular Sieve component, an idea supported by the data in Fig. 4. Compared with the primary products of F-T synthesis, coke is hydrogen deficient; formation of coke, therefore, like the formation of an aromatic liquid product, should be accompanied by the formation of hydrogen-rich products. Initially this catalyst was producing hydrogen-rich paraffins such as butane, but the selectivity switched to olefins as the catalyst's acidity decreased. Since none of the liquid samples was aromatic, the change in selectivity implies early coke formation.

The metal component of this catalyst gives a very stable operation. The Molecular Sieve component shows very high initial acid activity, which then deactivates rapidly due to coking. During most of this test the Molecular Sieve component had only a minor effect on the product, much smaller than with earlier samples.



# RUN 10011-17

1:1 H<sub>2</sub>:CO  
300 PSIG  
250°C

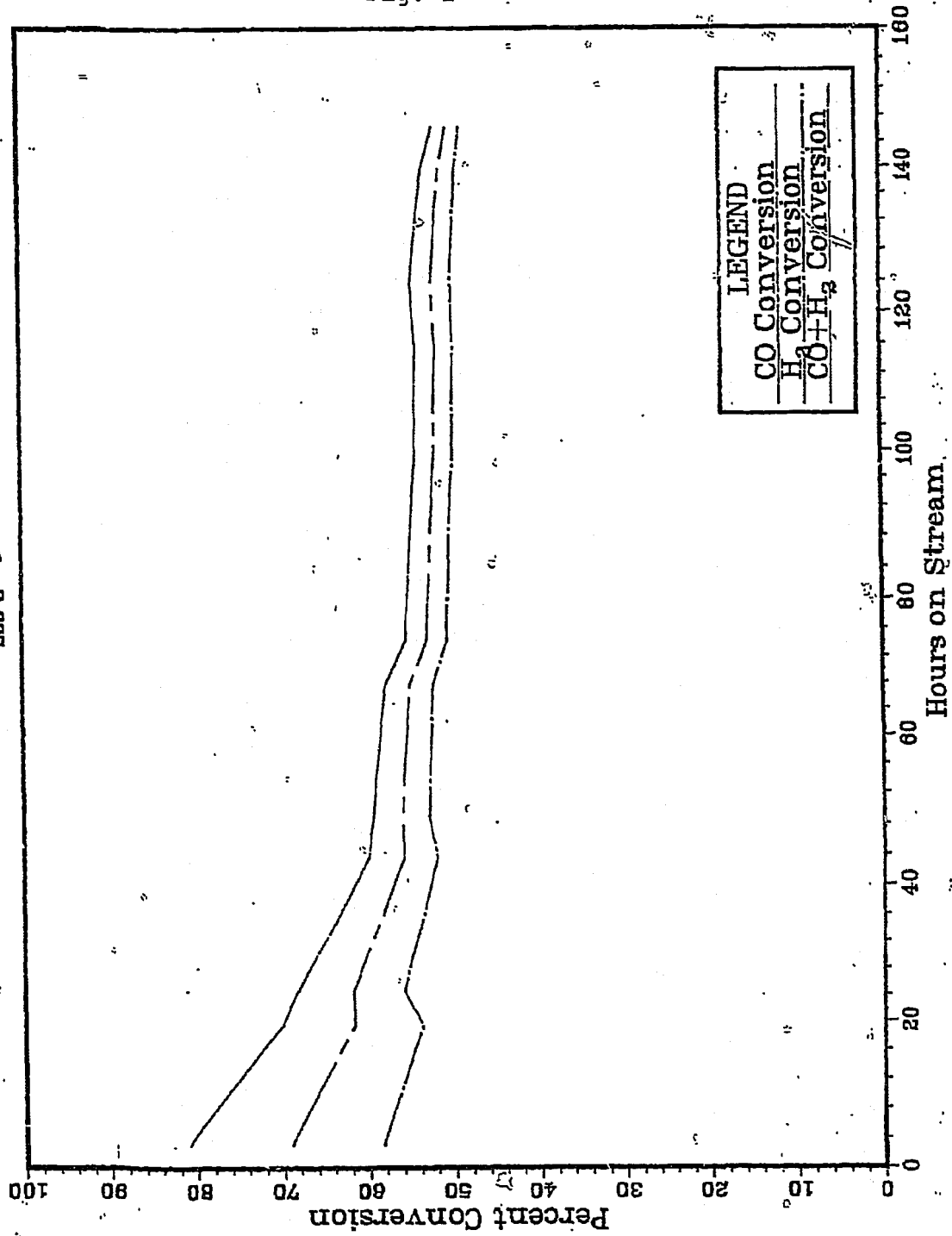


Fig. 1

RUN 10011-17

1:1 H<sub>2</sub>:CO  
300 PSIG  
250°C

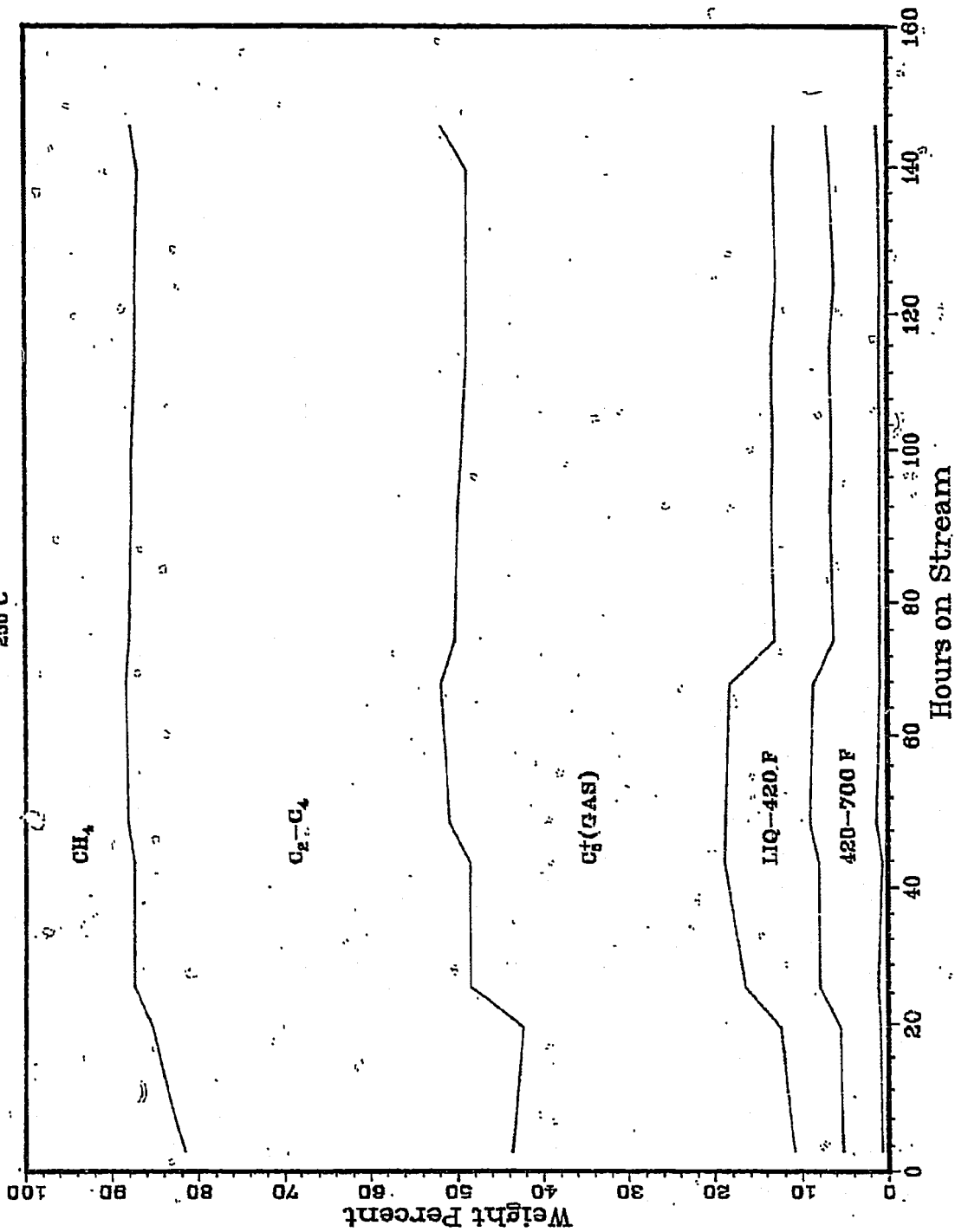


Fig. 2

RUN 10011-17

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250°C

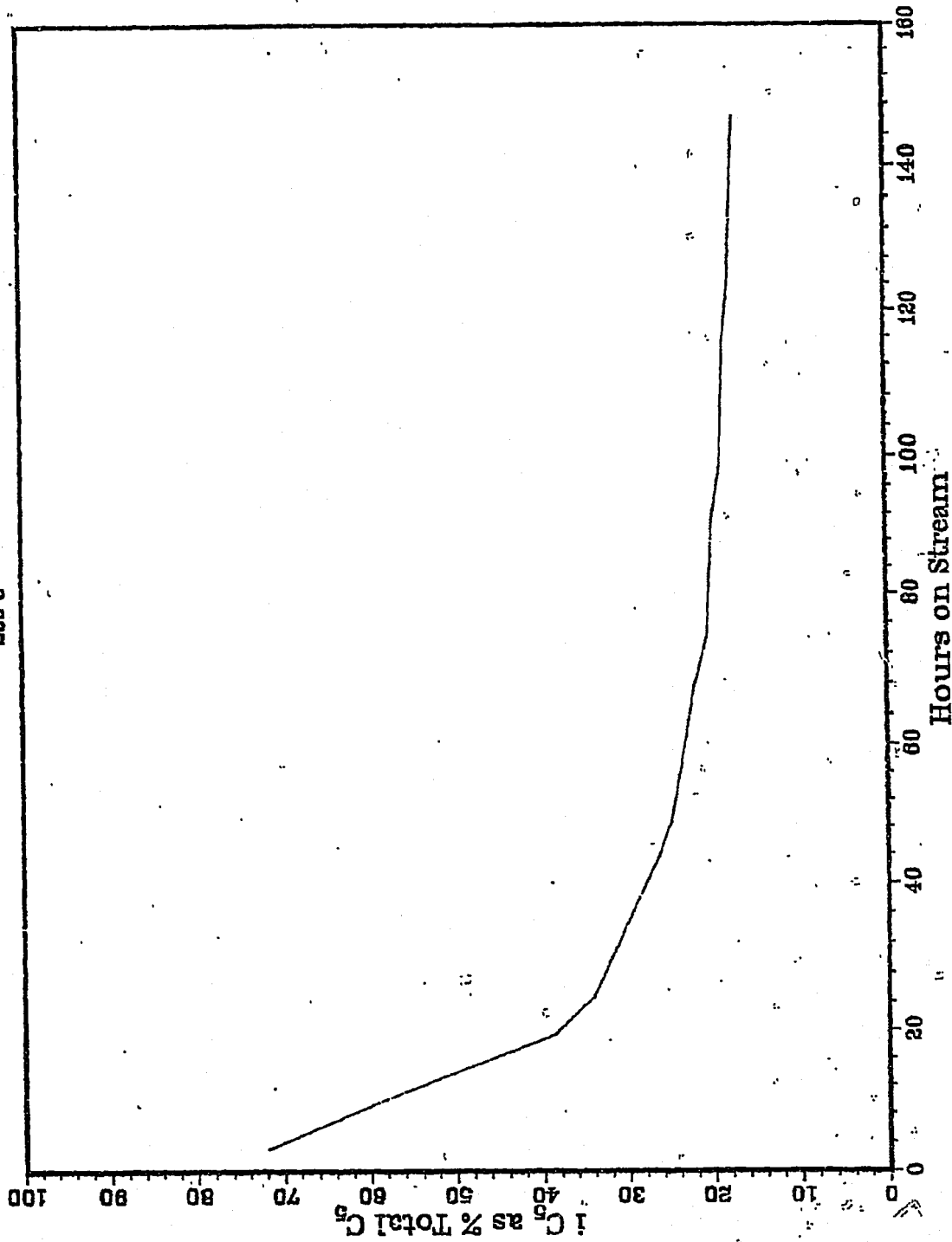


Fig. 3

RUN 10011-17

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300 PSIG  
250°C

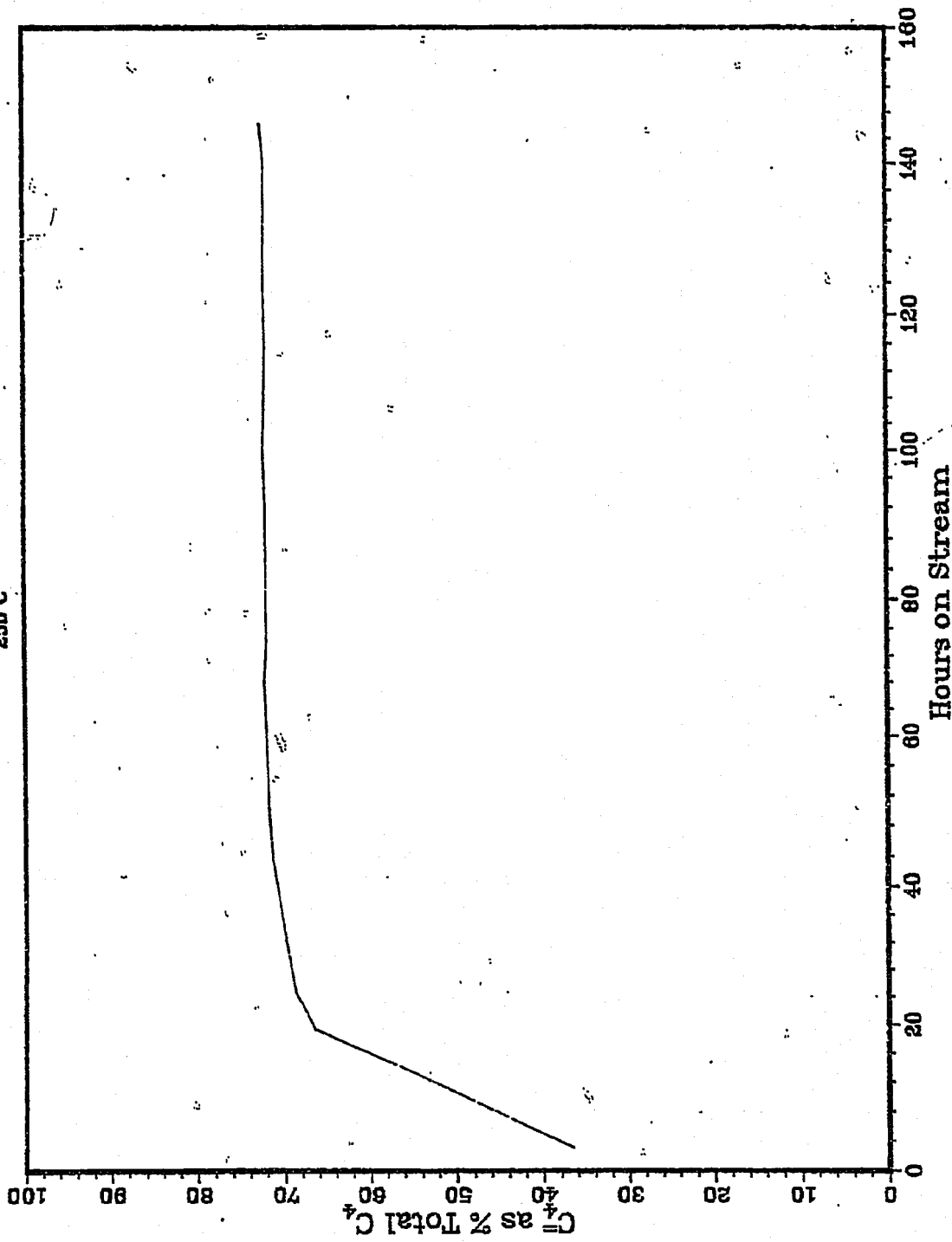


Fig. 4

Fig. 5

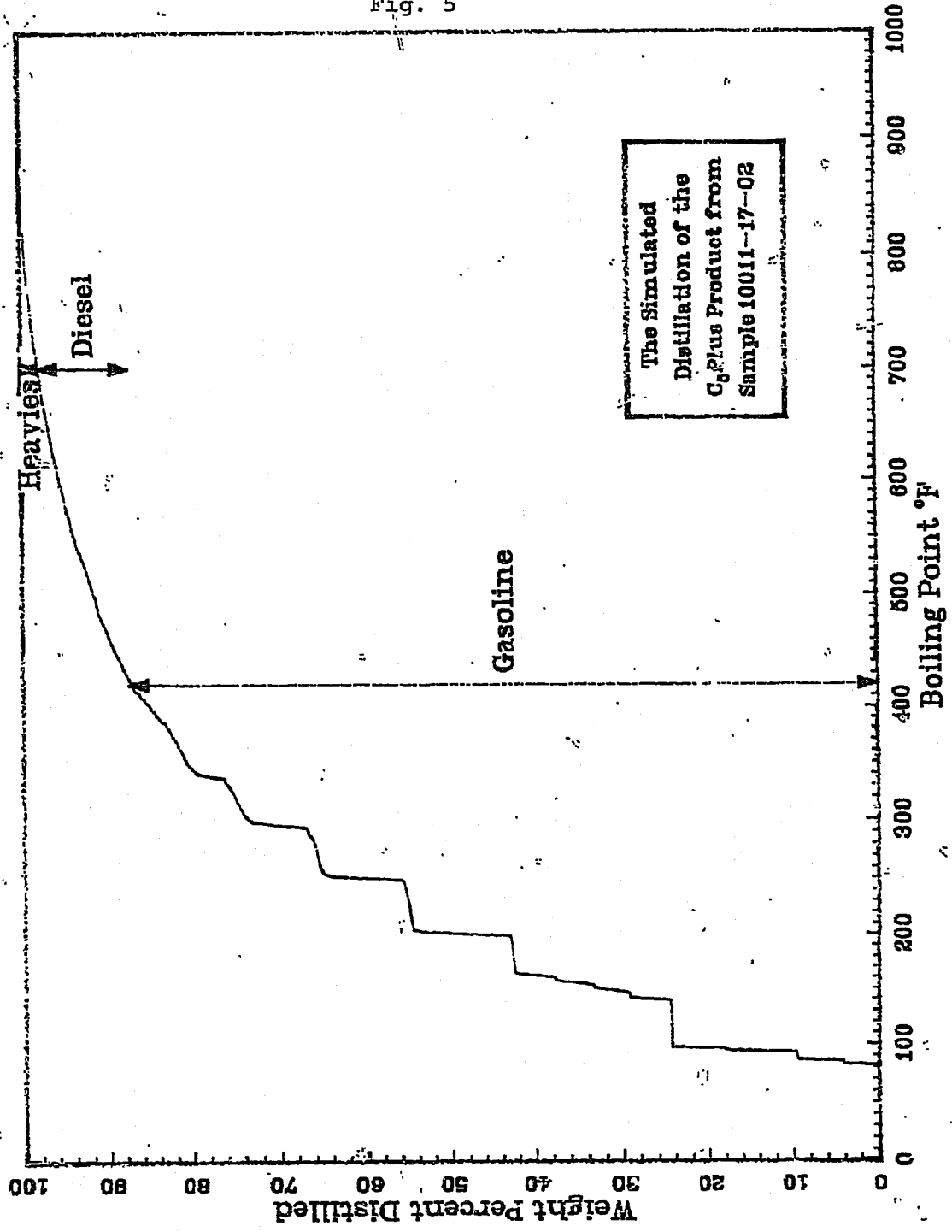


Fig. 6

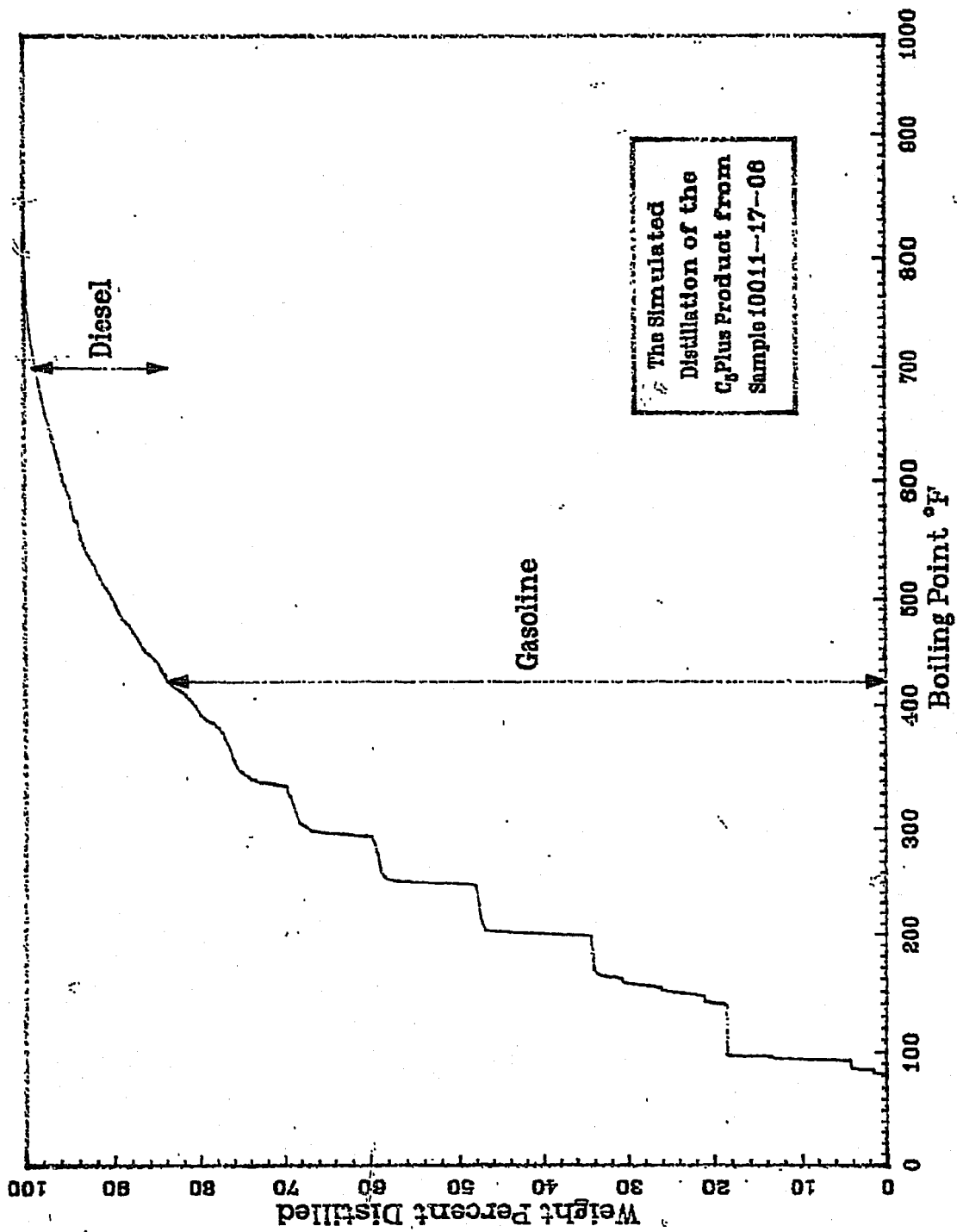


Fig. 7

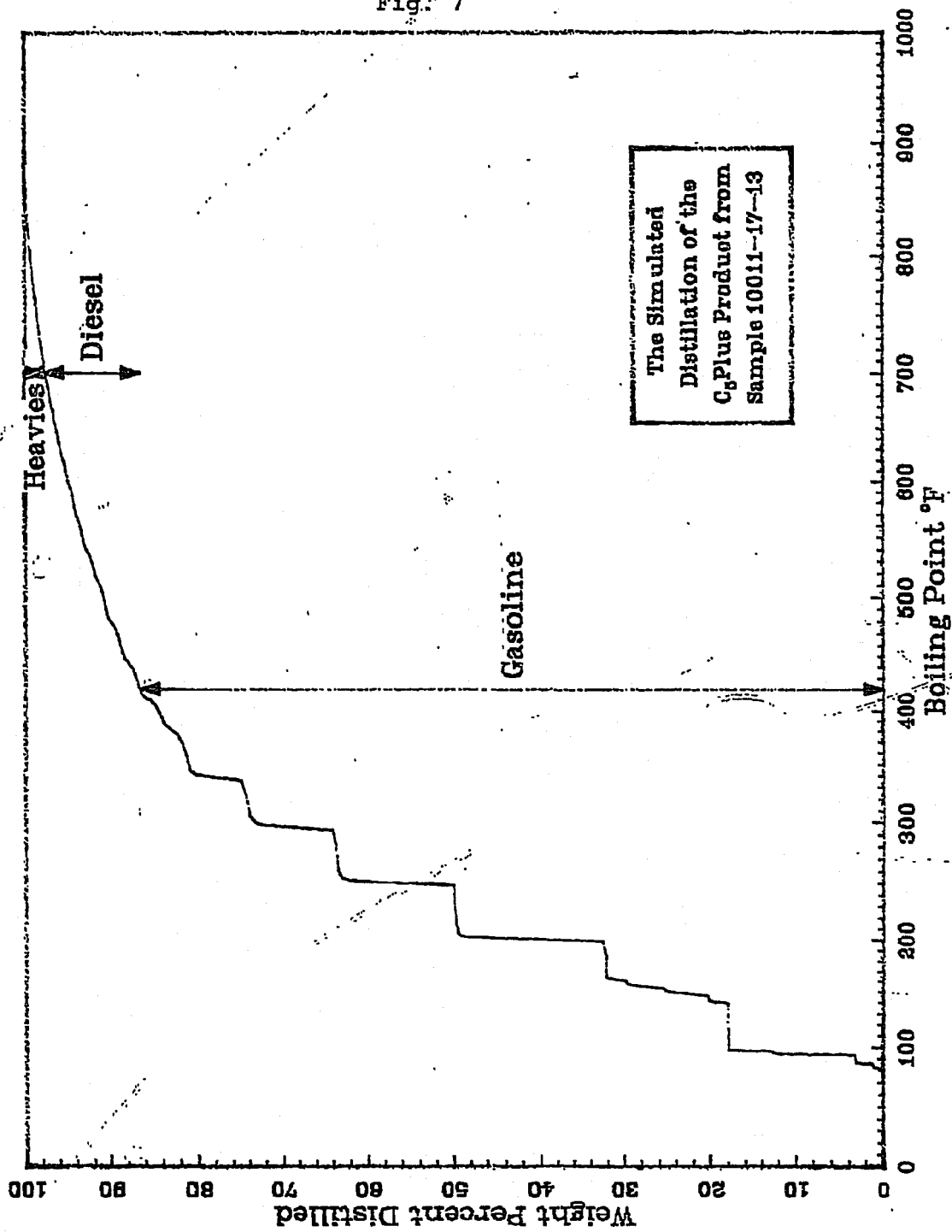


Fig. 8

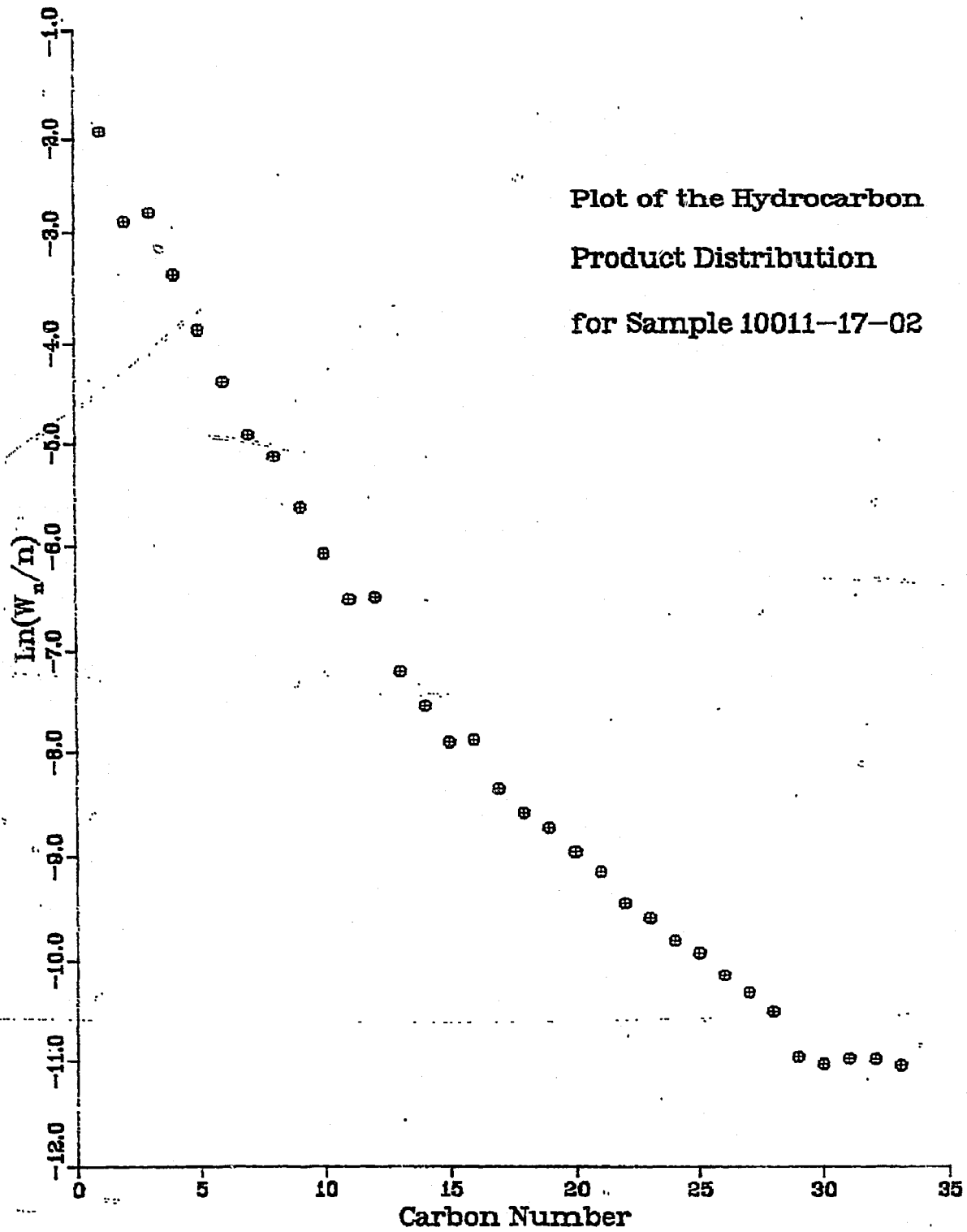




Fig. 9

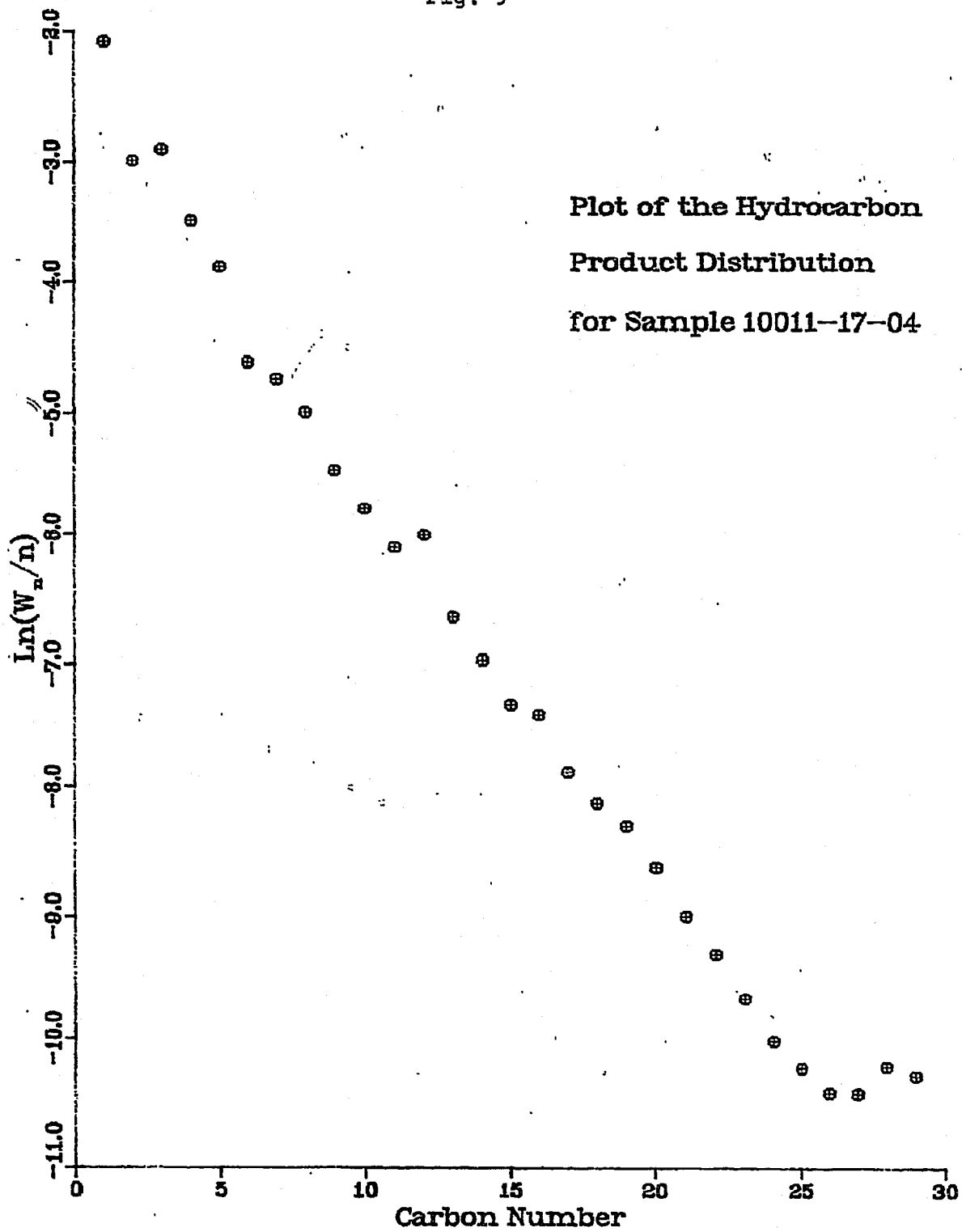


Fig. 10

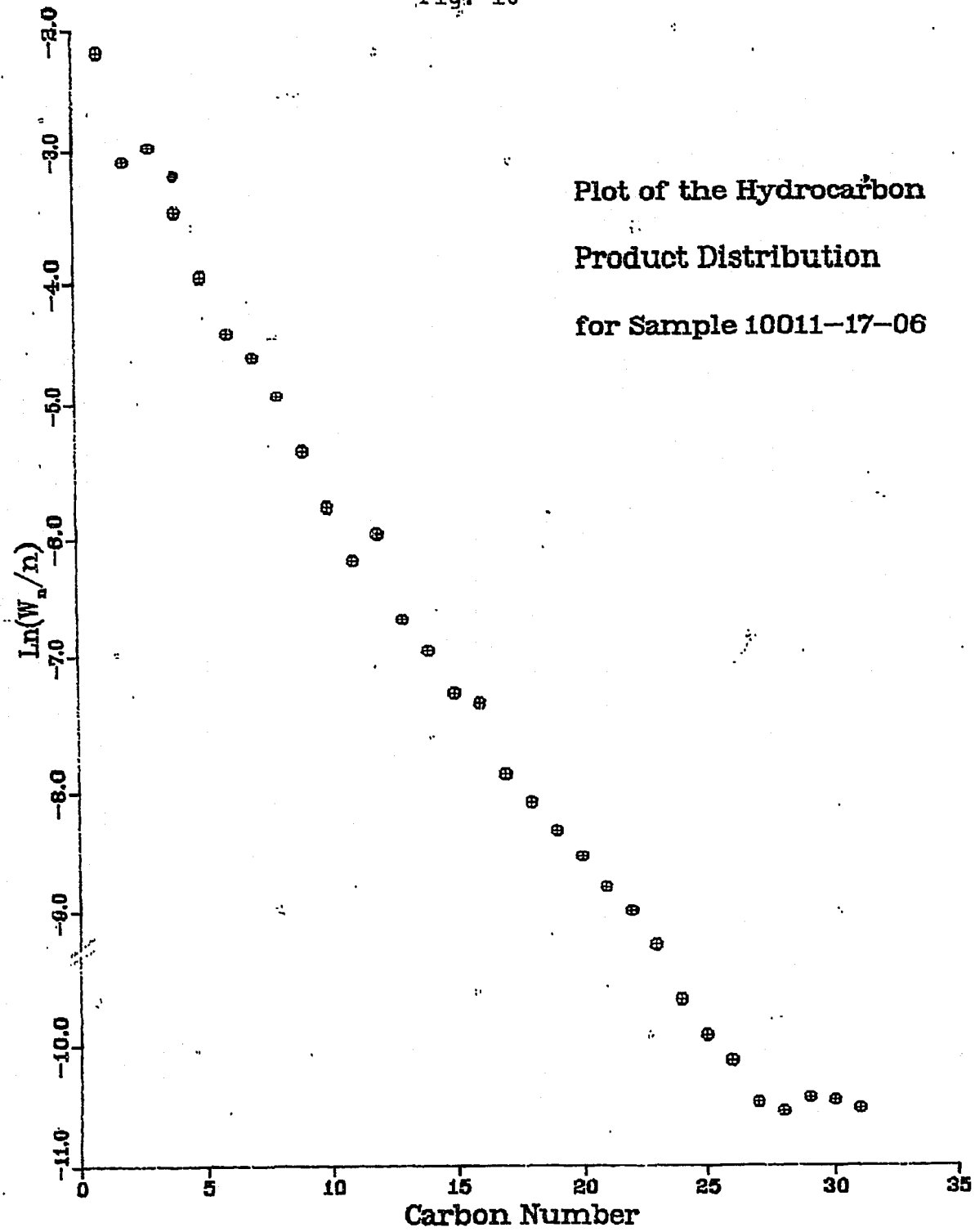


Fig. 11

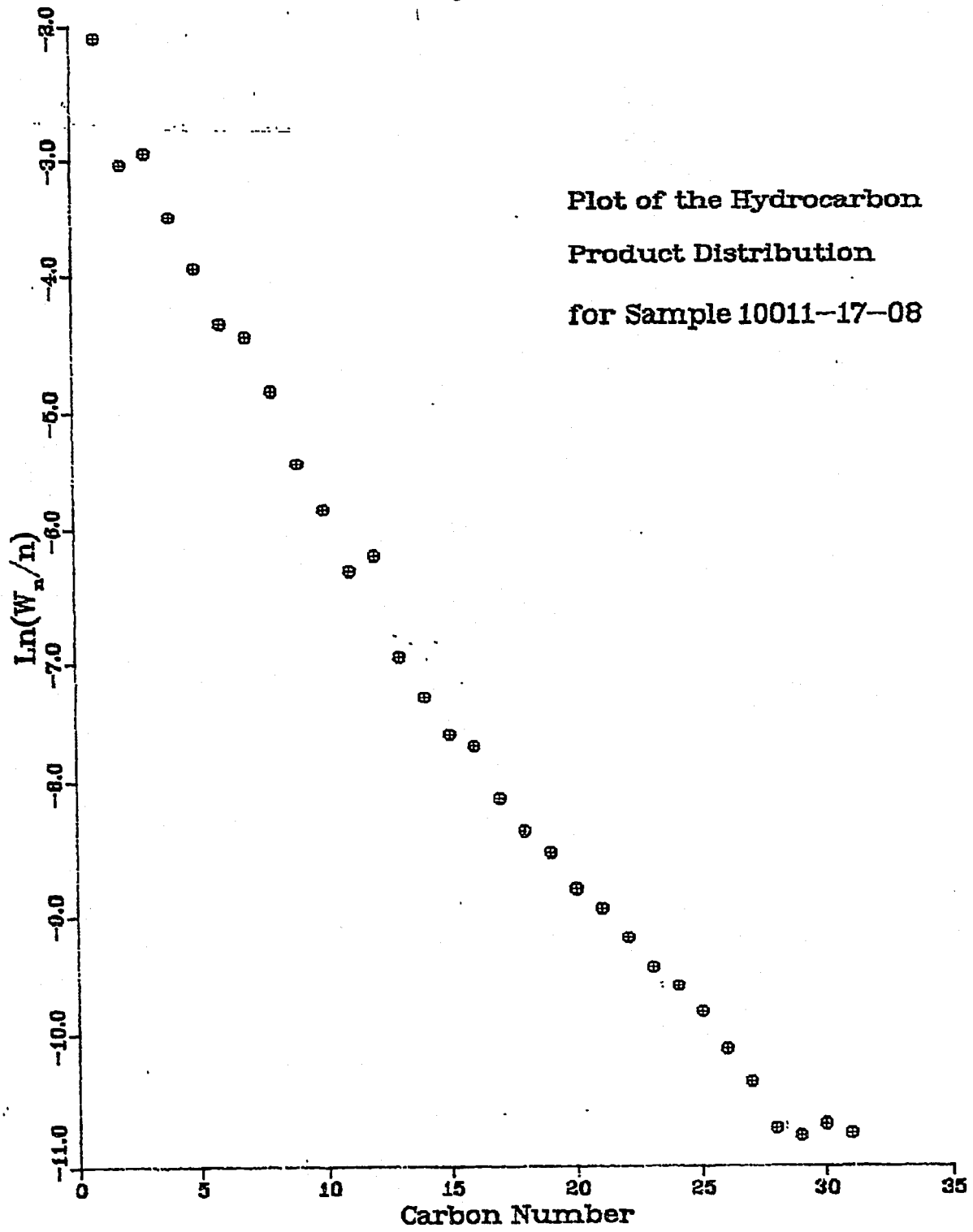


Fig. 12

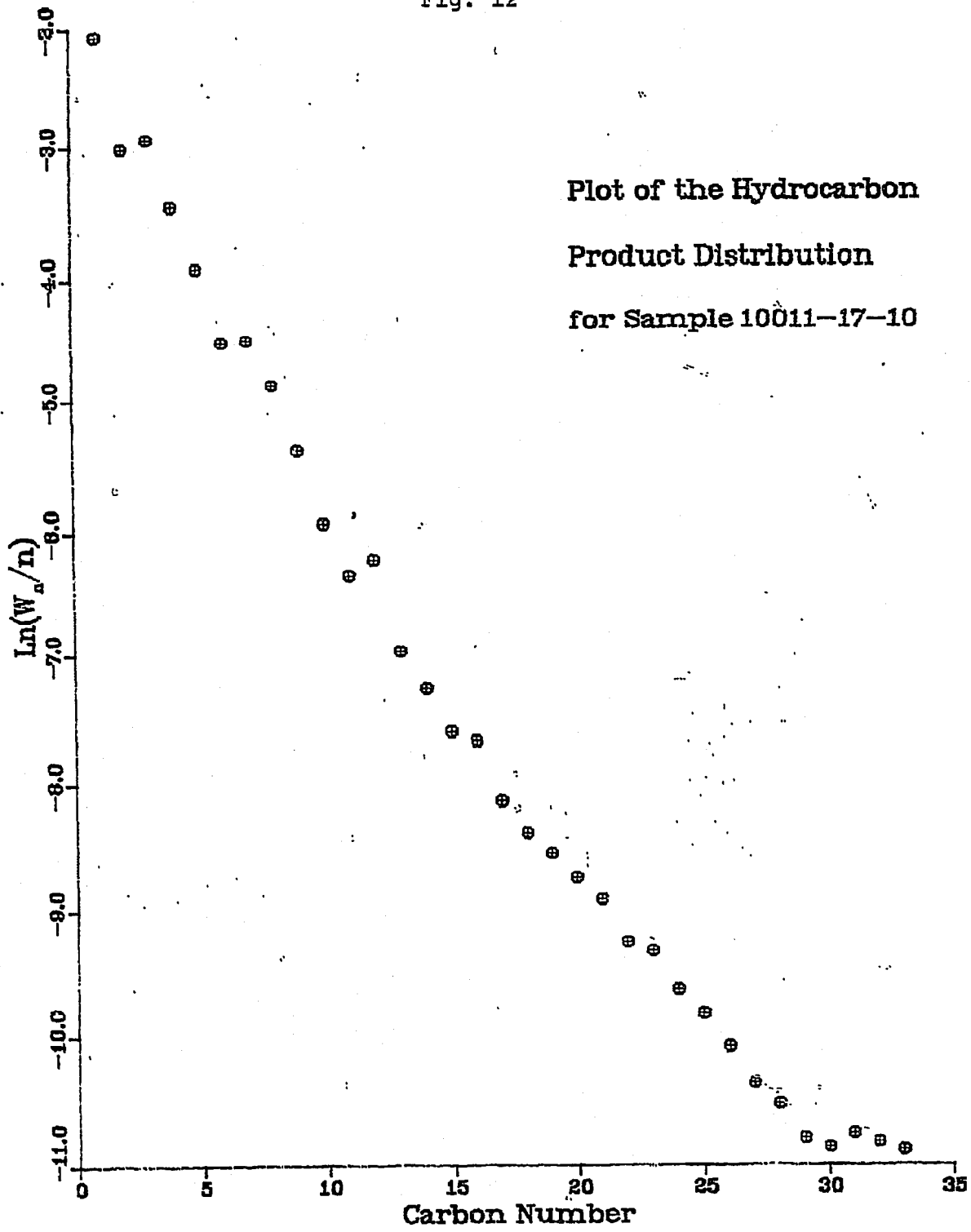


Fig. 13

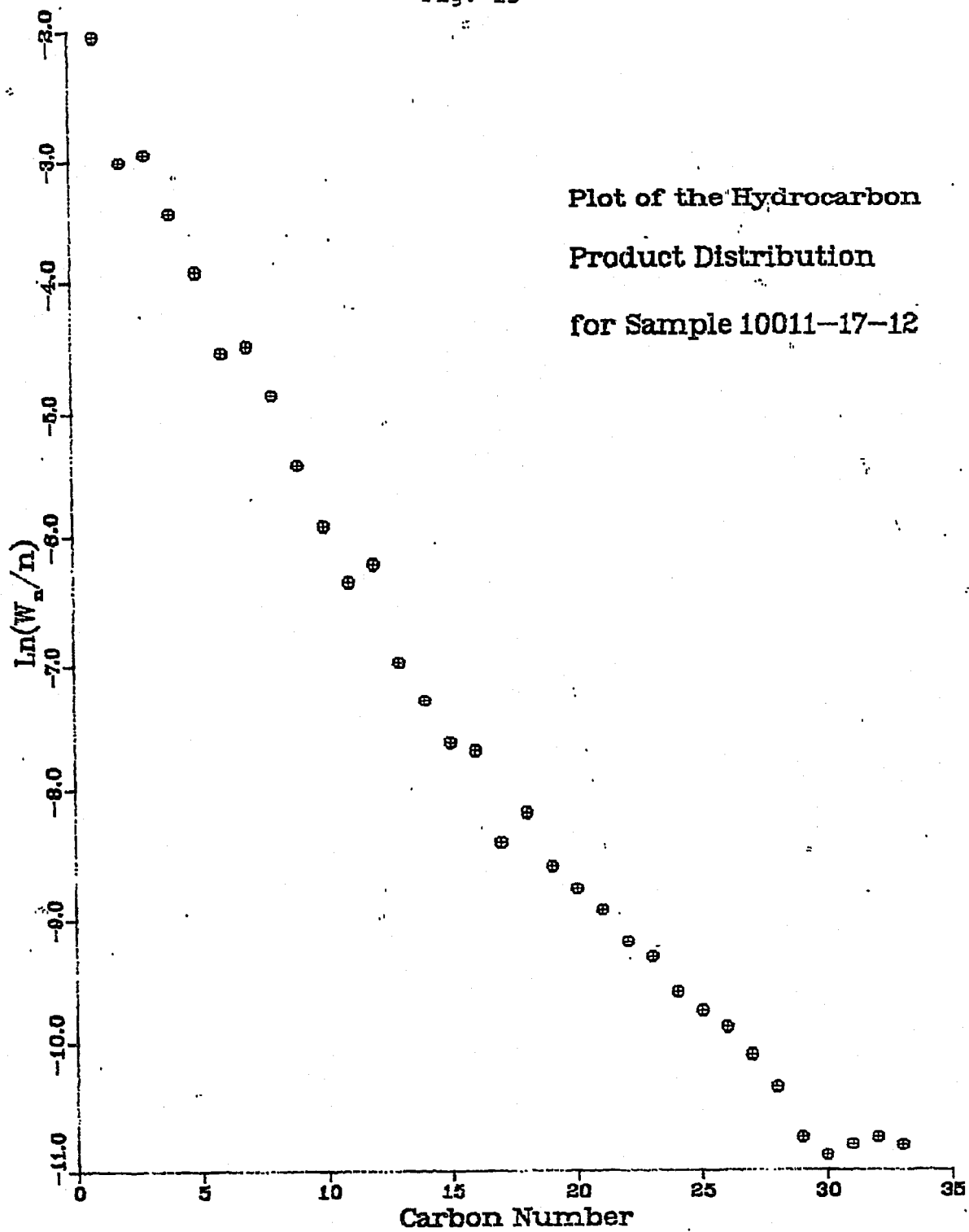
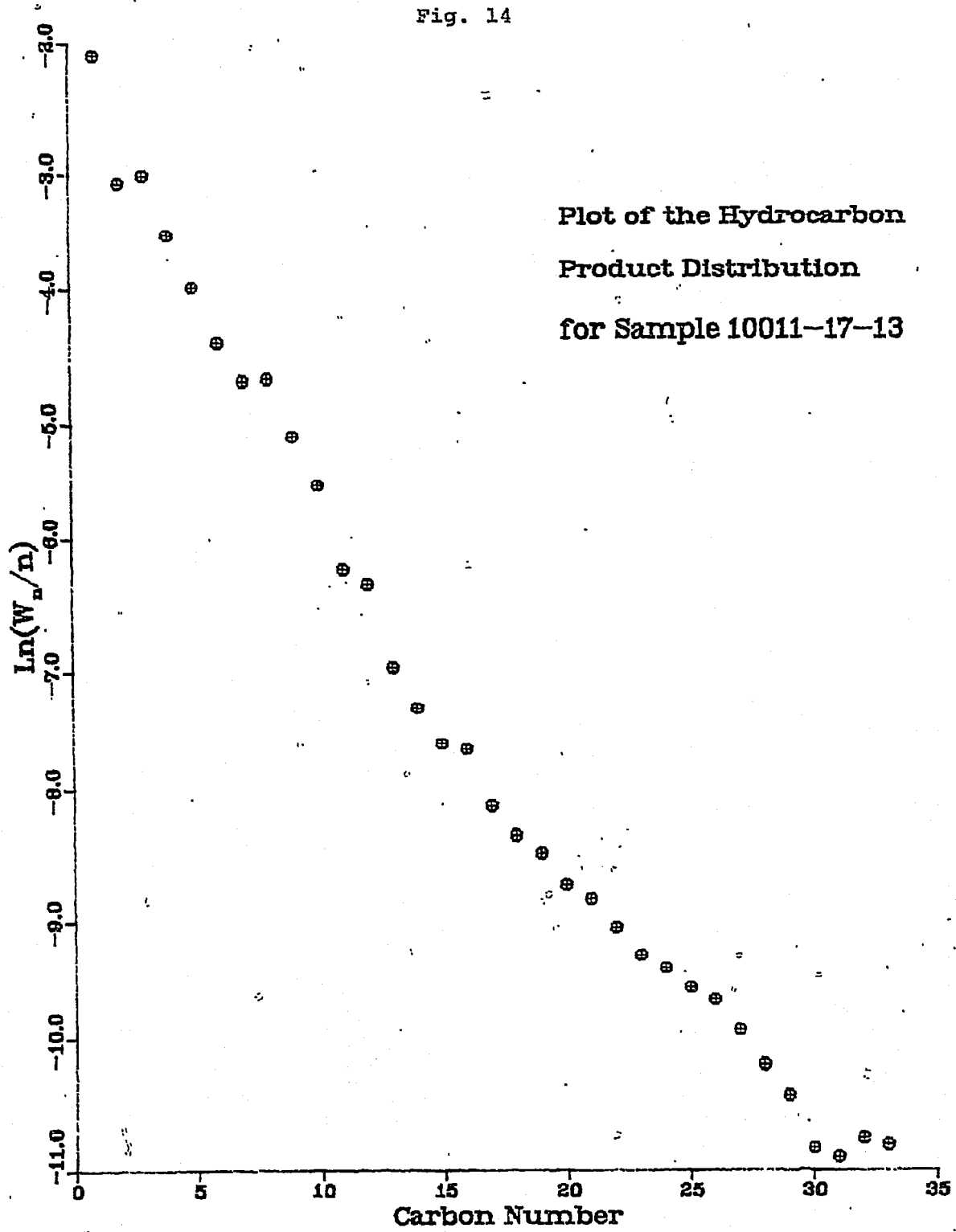
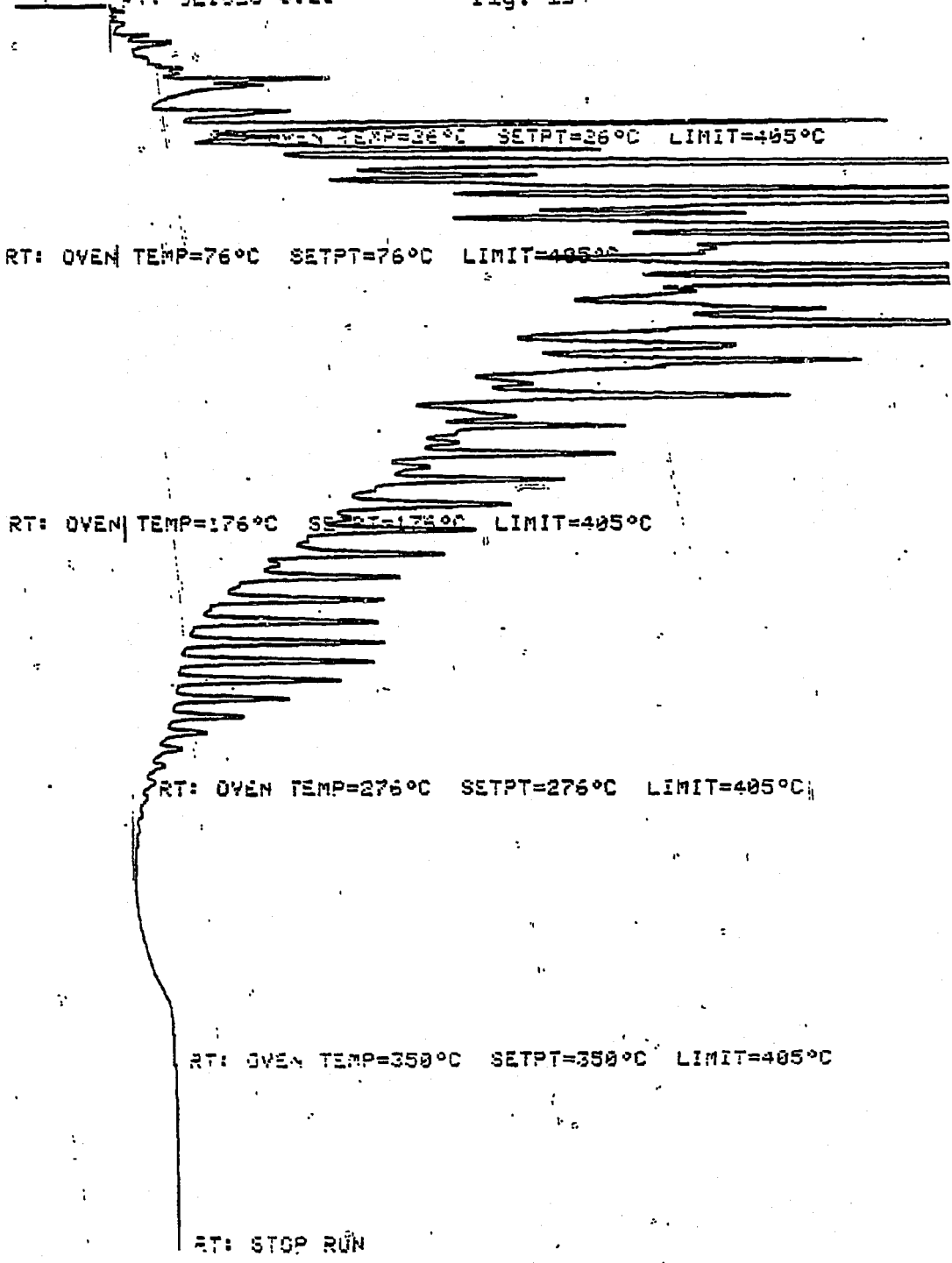


Fig. 14



RT: SLICES 8.20

Fig. 15.



ANALYTICAL CHEMISTRY CORPORATION BUFFALO NEW YORK

GC GC/MS 7400-110 9200 0025

SAMPLE: 19011-17-2L

013

RT: SLICES 0.20

Fig. 16

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C

RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C

RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE: 10011-17-4L

CHROMATIC CONTROLS CORPORATION BUFFALO NEW YORK

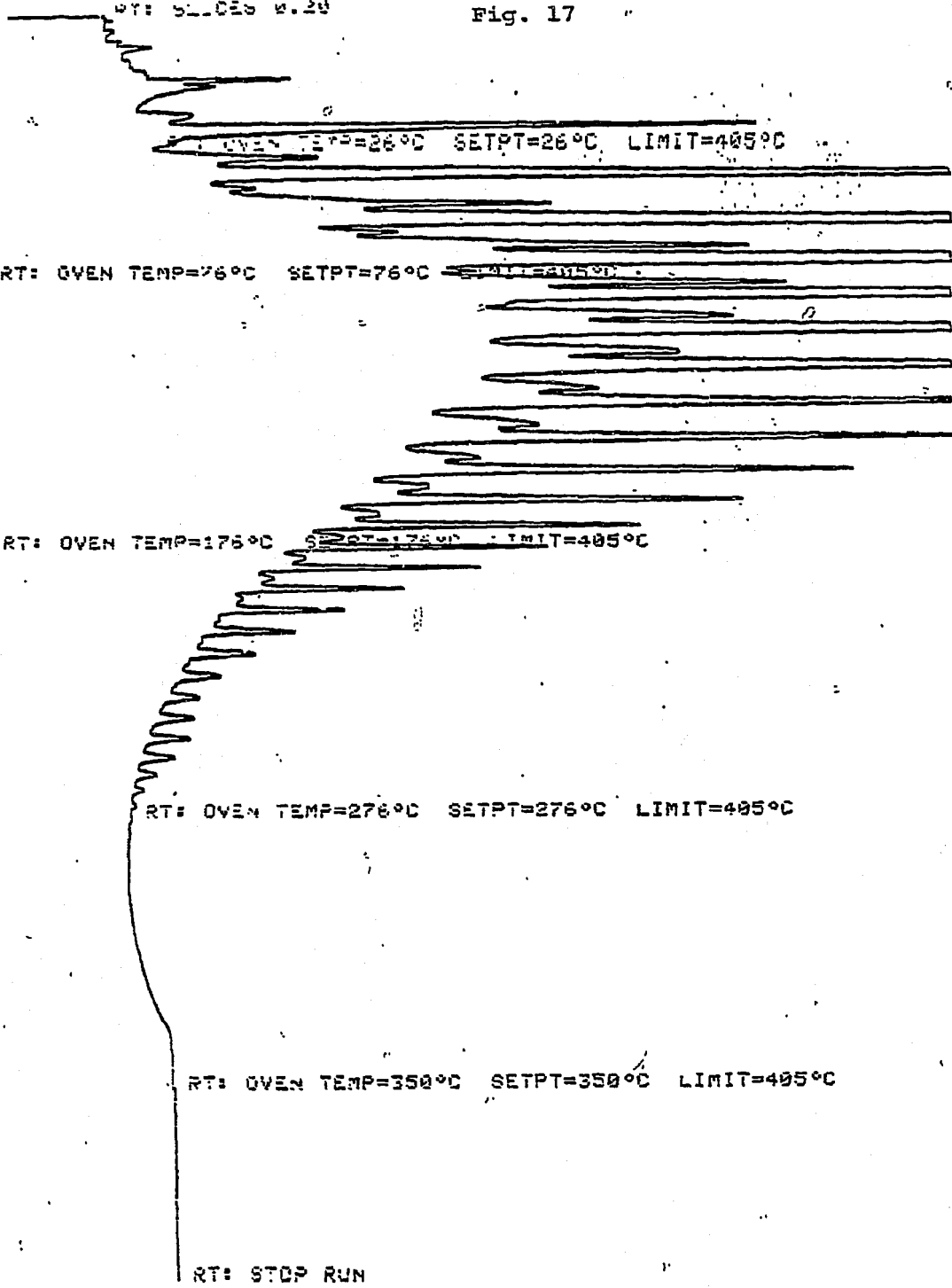
GC GCWAL 14001119 0710 0625

047



RT: 51-018 v.20

Fig. 17



GRAPHIC CONTROLS CORPORATION BUFFALO NEW YORK

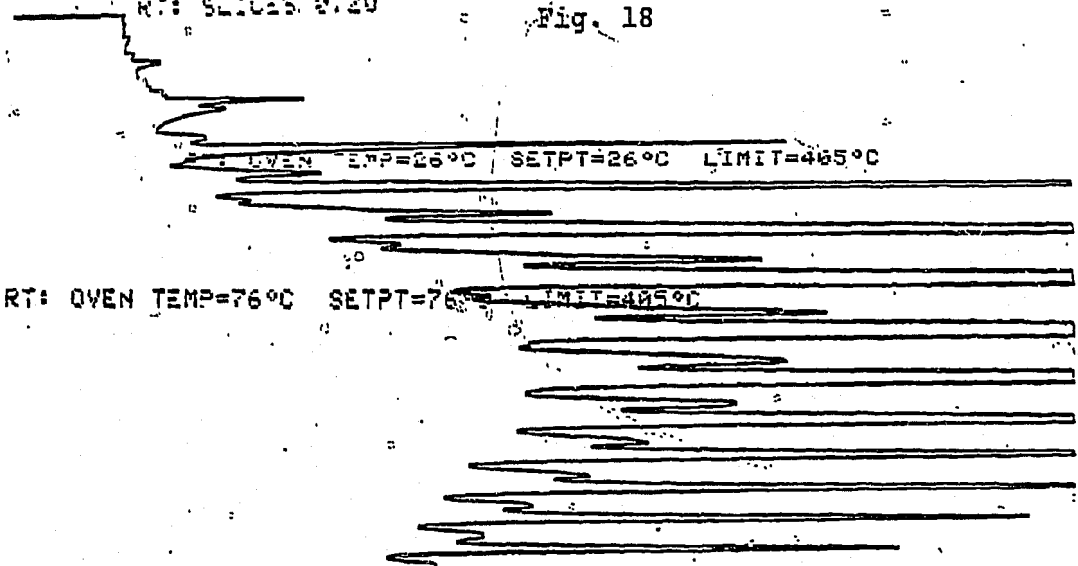
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051

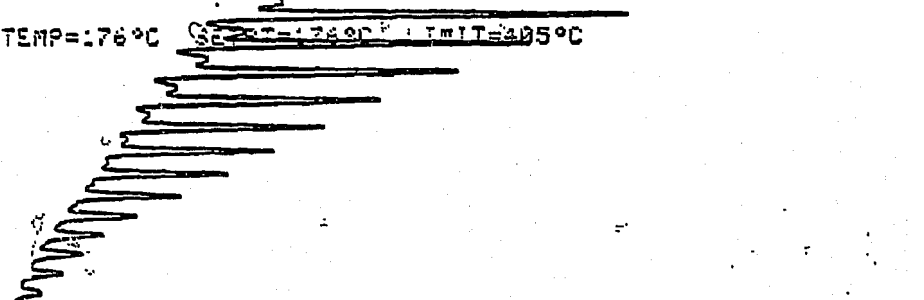
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Fig. 18

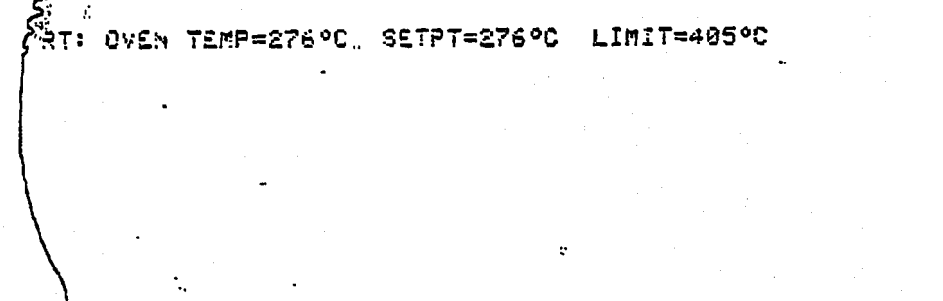


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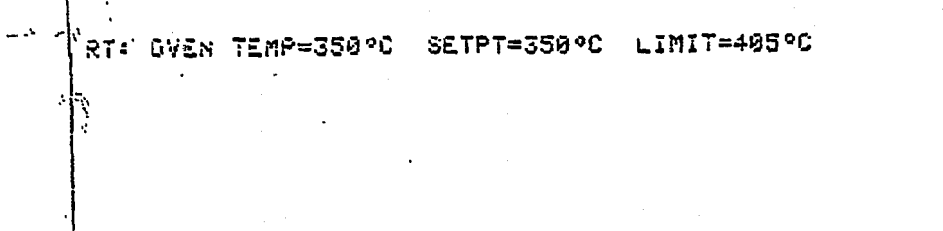
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RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C



RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C



RT: STOP RUN

SAMPLE:10011-17-8L

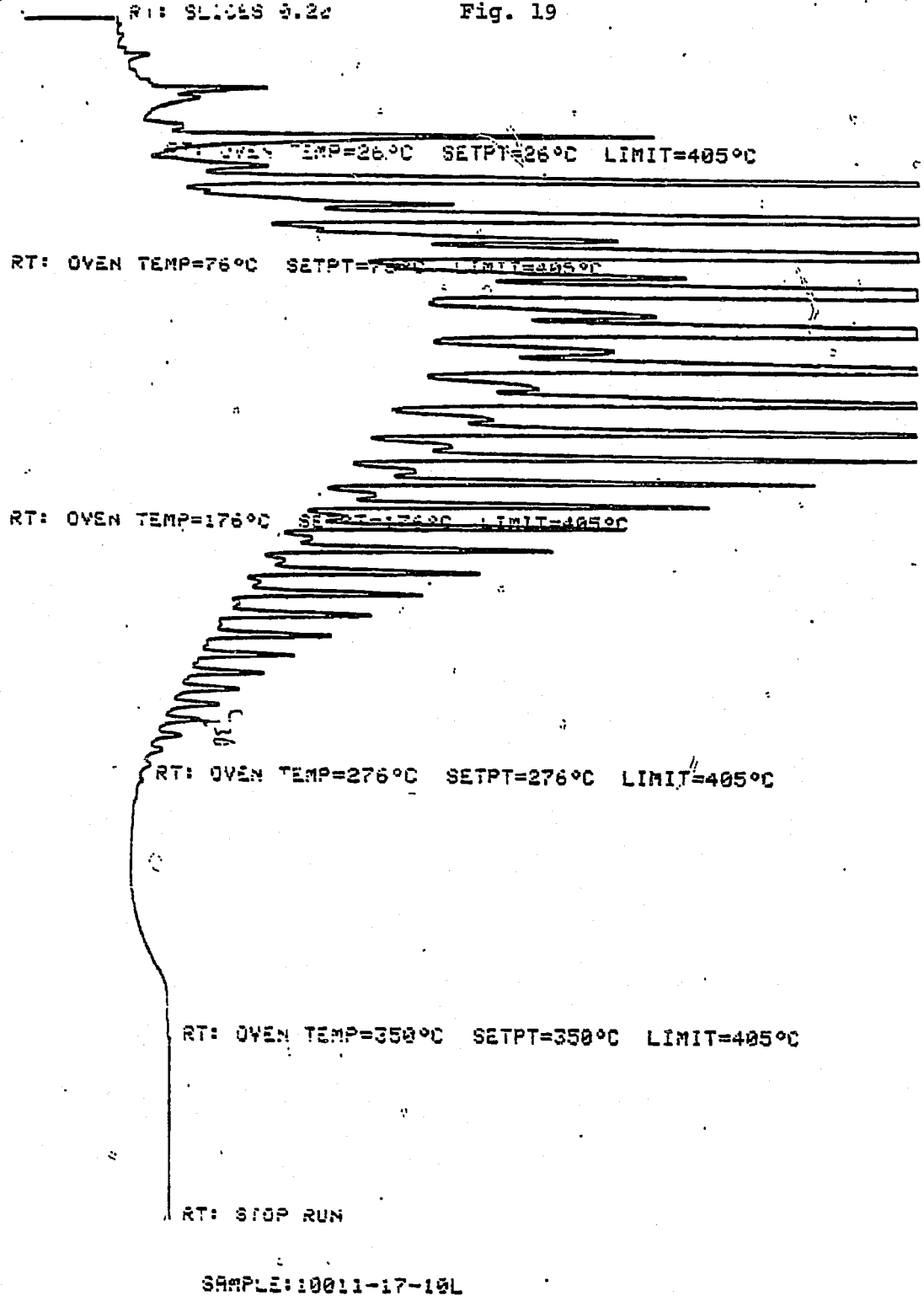
GRAPHIC CONTROL CORPORATION BUFFALO NEW YORK

GC CRYVAL 74103/11P 9270.003

055

RT: SLICES 0.20

Fig. 19



GRAPHIC CONTROLS CORPORATION RUI FALO MSN TEXAS

GC GC-VIA 74103/110 0220 0475

059

RT: SLICES 3.28

Fig. 20

RT: OVEN TEMP=26°C SETPT=26°C LIMIT=405°C

RT: OVEN TEMP=76°C SETPT=76°C LIMIT=405°C

RT: OVEN TEMP=176°C SETPT=176°C LIMIT=405°C

RT: OVEN TEMP=276°C SETPT=276°C LIMIT=405°C

RT: OVEN TEMP=350°C SETPT=350°C LIMIT=405°C

RT: STOP RUN

SAMPLE:1001:-17-12L

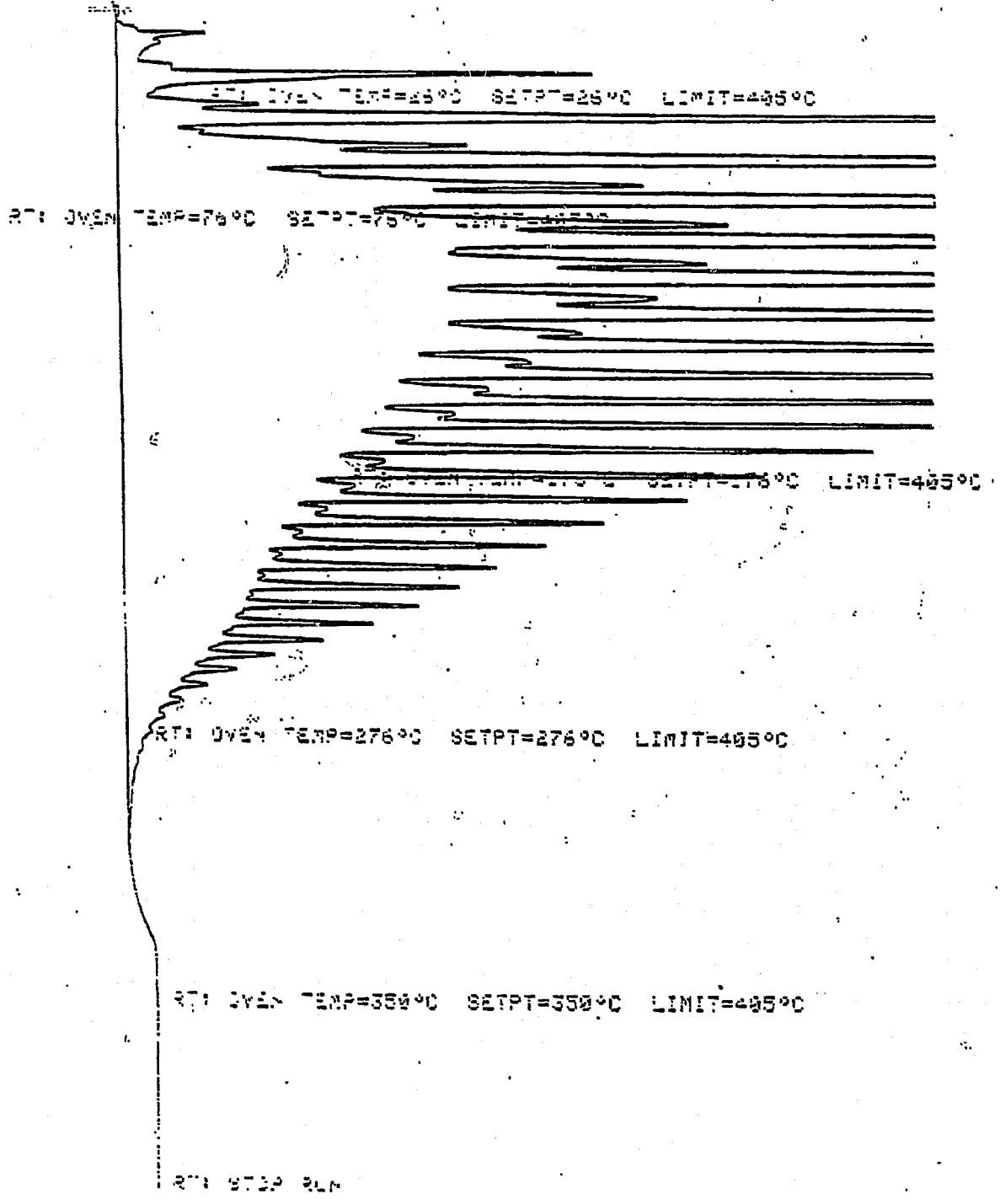
ASTRIC CONTROLS CORPORATION BUFFALO NEW YORK

GC GC-WAL 7403/11P 9720 0073

063

RT: 5.1000 0.20

Fig. 21



5.1000 0.20 10011-17-13L

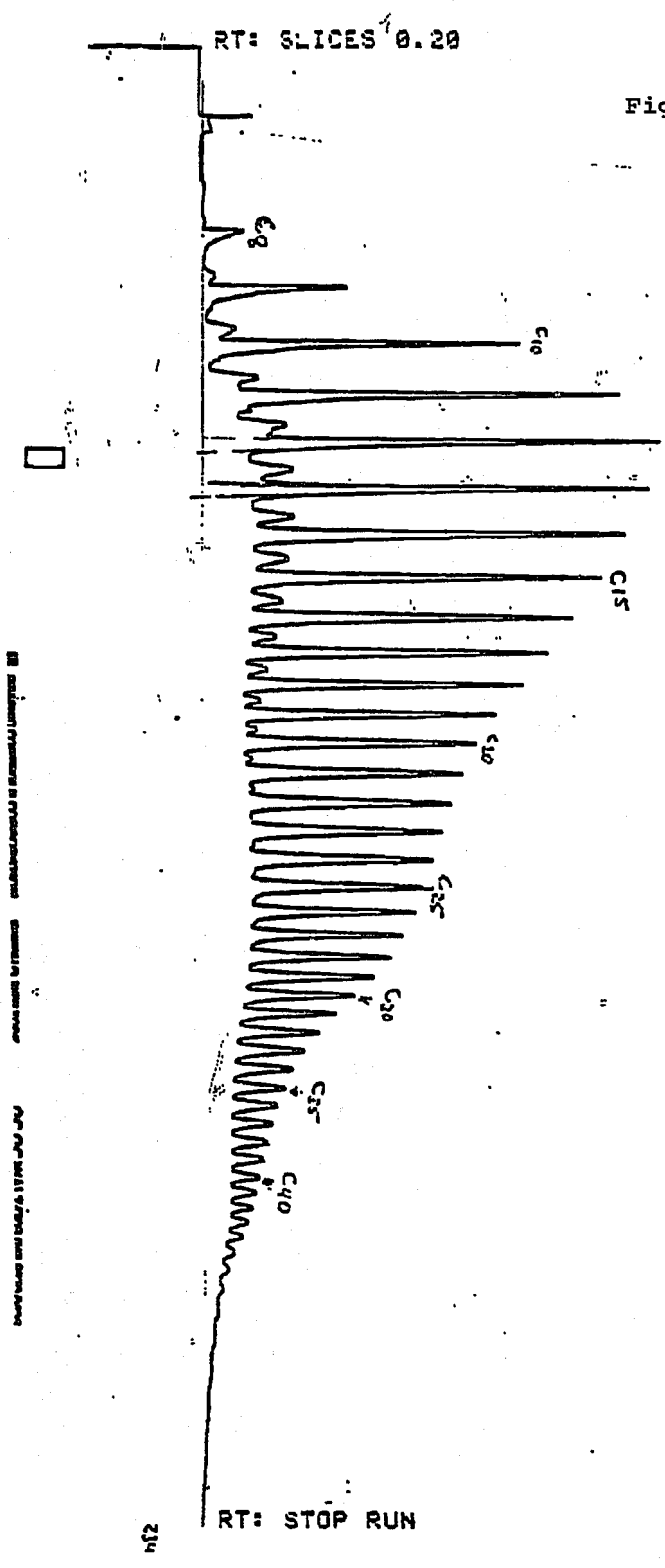


Fig. 22

TABLE 1A RESULT OF SYNGAS OPERATION

RUN NO. 10011-17  
 CATALYST FE+UCC-109 #10042-82 80CC 57.76GM (61.49GM AFTER RUN +3.73G)  
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-17-01	011-17-02	011-17-03	011-17-04	011-17-05
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	3.17	19.42	24.64	43.66	48.81
PRESSURE, PSIG	300	297	300	293	295
TEMP. C	251	251	250	250	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	3.17	19.42	5.22	24.24	5.15
EFFLNT GAS LITER	40.25	258.00	70.64	342.05	74.46
GM AQUEOUS LAYER	2.25	13.80	5.28	24.52	5.47
GM OIL	0.90	5.52	2.15	10.00	2.26
MATERIAL BALANCE					
GM ATOM CARBON %	86.28	87.13	91.12	90.07	93.74
GM ATOM HYDROGEN %	96.81	91.68	98.69	96.62	100.50
GM ATOM OXYGEN %	94.26	94.40	97.01	96.11	97.68
RATIO CHX/(H2O+CO2)	0.8185	0.8147	0.8556	0.8358	0.8932
RATIO X IN CHX	2.5916	2.4556	2.3916	2.3793	2.3607
USAGE H2/CO PRDCT	0.7656	0.7622	0.8482	0.8809	0.9226
RATIO CO2/(H2O+CO2)	0.7728	0.7427	0.6688	0.6304	0.6142
K SHIFT IN EFFLNT	8.38	4.69	3.03	2.19	1.98
CONVERSION					
ON CO %	81.09	70.11	68.27	59.91	59.31
ON H2 %	58.48	53.81	55.99	51.96	52.85
ON CO+H2 %	69.13	61.75	61.88	55.80	55.97
PRDCT SELECTIVITY, WT %					
CH4	18.34	14.65	12.62	12.57	11.96
C2 HC'S	11.13	11.11	9.71	10.07	9.42
C3H8	8.48	7.25	6.05	5.51	5.17
C3H6=	5.57	11.02	10.30	11.05	10.46
C4H10	8.21	4.67	4.12	3.64	3.53
C4H8=	4.58	8.90	8.73	8.70	8.58
C5H12	9.33	4.41	4.05	3.55	3.52
C5H10=	2.78	5.97	6.11	6.85	6.93
C6H14	6.89	3.89	3.64	2.64	2.68
C6H12= & CYCLO'S	1.56	3.66	3.93	3.14	3.17
C7+ IN GAS	12.19	12.04	14.17	13.42	15.83
LIQ HC'S	10.93	12.43	16.57	18.85	18.75

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	56.32	57.60	51.53	51.55	49.12
C5 -420 F	38.43	36.96	40.52	40.35	41.88
420-700 F	4.48	4.55	6.79	7.47	7.69
700-END PT	0.76	0.90	1.16	0.63	1.31
C5+-END PT	43.68	42.40	48.47	48.45	50.88
ISO/NORMAL MOLE RATIO					
C4	1.1280	0.3075	0.2673	0.2051	0.1883
C5	2.5606	0.6324	0.5177	0.3603	0.3320
C6	3.1107	1.1062	0.9836	0.3652	0.3088
C4=	0.0625	0.0764	0.0791	0.0851	0.0853
PARAFFIN/OLEFIN RATIO					
C3	1.4526	0.6280	0.5604	0.4756	0.4719
C4	1.7305	0.5061	0.4553	0.4039	0.3972
C5	3.2577	0.7188	0.6448	0.5040	0.4929
LIQ HC COLLECTION					
PHYS. APPEARANCE	---	YL-BR OIL	---	CLDY OIL	---
DENSITY	---	0.784	---	0.776	---
N, REFRACTIVE INDEX	---	1.4427	---	1.4355	---
SIMULT'D DISTILATN					
10 WT % @ DEG F	---	256	---	256	---
16	---	291	---	295	---
50	---	404	---	404	---
84	---	594	---	553	---
90	---	657	---	606	---
RANGE(16-84 %)	---	303	---	258	---
WT % @ 420 F	---	56.20	---	57.00	---
WT % @ 700 F	---	92.80	---	96.65	---



TABLE 1B

## RESULT OF SYNGAS OPERATION

RUN NO.	10011-17				
CATALYST	FE+UCC-109 #10042-82 80CC 57.76GM (61.49GM AFTER RUN +3.73GM)				
FEED	H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV				
RUN & SAMPLE NO.	10011-17-06	011-17-07	011-17-08	011-17-09	011-17-10
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	67.58	74.25	91.67	99.00	115.33
PRESSURE, PSIG	302	297	300	293	298
TEMP. C	250	250	250	250	251
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	23.92	6.67	24.09	7.33	23.66
EFFLNT GAS LITER	356.96	104.16	375.36	114.44	371.23
GM AQUEOUS LAYER	25.39	6.96	25.15	7.58	24.46
GM OIL	10.49	2.04	7.38	2.21	7.13
MATERIAL BALANCE					
GM ATOM CARBON %	96.35	98.47	97.48	97.07	97.25
GM ATOM HYDROGEN %	103.22	104.82	104.05	104.25	104.16
GM ATOM OXYGEN %	98.88	101.50	100.80	100.05	100.75
RATIO CHX/(H2O+CO2)	0.9302	0.9157	0.9062	0.9147	0.9004
RATIO X IN CHX	2.3537	2.3669	2.3737	2.3768	2.3845
USAGE H2/CO PRDCT	0.9478	0.9465	0.9514	0.9602	0.9530
RATIO CO2/(H2O+CO2)	0.6058	0.6047	0.5989	0.5957	0.5980
K SHIFT IN EFFLNT	1.86	1.80	1.75	1.73	1.74
CONVERSION					
ON CO %	57.82	55.47	54.67	54.25	54.06
ON H2 %	52.31	50.69	50.25	49.88	49.70
ON CO+H2 %	54.97	53.01	52.39	51.99	51.81
PRDCT SELECTIVITY, WT %					
CH4	11.69	12.10	12.43	12.47	12.83
C2 HC'S	9.07	9.44	9.63	9.63	9.85
C3H8	5.07	5.21	5.20	5.27	5.27
C3H6=	10.42	10.73	10.62	10.61	10.75
C4H10	3.43	3.57	3.53	3.61	3.59
C4H8=	8.58	8.82	8.77	9.02	8.88
C5H12	3.48	3.62	3.51	3.69	3.62
C5H10=	6.09	6.36	6.22	6.38	6.34
C6H14	3.49	3.56	3.50	3.74	3.57
C6H12= & CYCLO'S	4.17	4.28	4.14	3.31	3.15
C7+ IN GAS	16.19	19.24	19.03	18.98	18.75
LIQ HC'S	18.30	13.08	13.42	13.29	13.40

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	48.27	49.86	50.17	50.62	51.16
C5 -420 F	43.13	43.86	43.22	43.01	42.14
420-700 F	7.71	5.36	5.72	5.45	5.73
700-END PT	0.90	0.92	0.89	0.93	0.97
C5*-END PT	51.73	50.14	49.83	49.38	48.84
ISO/NORMAL MOLE RATIO					
C4	0.1676	0.1601	0.1403	0.1433	0.1389
C5	0.2856	0.2610	0.2505	0.2361	0.2301
C6	0.6168	0.5842	0.5556	0.5287	0.5191
C4=	0.0885	0.0876	0.0915	0.0898	0.0905
PARAFFIN/OLEFIN RATIO					
C3	0.4644	0.4635	0.4671	0.4742	0.4683
C4	0.3860	0.3904	0.3882	0.3858	0.3899
C5	0.5559	0.5532	0.5475	0.5627	0.5550
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLDY OIL	---	CLEAR OIL	---	CLEAR OIL
DENSITY	0.773	---	0.775	---	0.772
N, REFRACTIVE INDEX	1.4355	---	1.4345	---	1.4337
SIMULT'D DISTILATN					
10 WT % @ DEG F	277	---	288	---	292
16	302	---	304	---	305
50	413	---	417	---	420
84	578	---	599	---	606
90	634	---	658	---	666
RANGE(16-84 %)	276	---	295	---	301
WT % @ 420 F	53.00	---	50.75	---	50.00
WT % @ 700 F	95.11	---	93.40	---	92.77

TABLE 1C

## RESULT OF SYNGAS OPERATION

RUN NO. 10011-17  
 CATALYST FE+UCC-109 #10042-82 80CC 57.76GM (61.49GM AFTER RUN +3.73GM)  
 FEED H<sub>2</sub>:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10011-17-11 =====	011-17-12 =====	011-17-13 =====
FEED H <sub>2</sub> :CO:AR	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	123.50	139.42	146.25
PRESSURE, PSIG	302	303	293
TEMP. C	251	250	249
FEED CC/MIN	400	400	400
HOURS FEEDING	8.17	24.09	6.83
EFFLNT GAS LITER	127.80	379.60	108.86
GM AQUEOUS LAYER	8.42	24.83	6.88
GM OIL	2.39	7.04	2.01
MATERIAL BALANCE			
GM ATOM CARBON %	97.29	97.15	98.14
GM ATOM HYDROGEN %	104.06	103.73	104.86
GM ATOM OXYGEN %	100.81	100.89	99.86
RATIO CHX/(H <sub>2</sub> O+CO <sub>2</sub> )	0.9002	0.8923	0.9481
RATIO X IN CHX	2.3853	2.3890	2.3649
USAGE H <sub>2</sub> /CO PRODT	0.9483	0.9544	0.9872
RATIO CO <sub>2</sub> /(H <sub>2</sub> O+CO <sub>2</sub> )	0.6019	0.5950	0.5835
K SHIFT IN EFFLNT	1.78	1.70	1.59
CONVERSION			
ON CO %	54.53	53.24	51.88
ON H <sub>2</sub> %	49.95	49.30	48.75
ON CO+H <sub>2</sub> %	52.16	51.21	50.27
PRDT SELECTIVITY, WT %			
CH <sub>4</sub>	12.84	13.09	12.32
C <sub>2</sub> HC'S	9.80	9.90	9.30
C <sub>3</sub> H <sub>8</sub>	5.32	5.27	4.88
C <sub>3</sub> H <sub>6</sub> =	10.70	10.62	9.96
C <sub>4</sub> H <sub>10</sub>	3.60	3.56	3.34
C <sub>4</sub> H <sub>8</sub> =	8.96	8.82	8.48
C <sub>5</sub> H <sub>12</sub>	3.65	3.59	3.38
C <sub>5</sub> H <sub>10</sub> =	6.42	6.26	5.95
C <sub>6</sub> H <sub>14</sub>	3.69	3.53	3.44
C <sub>6</sub> H <sub>12</sub> = & CYCLO'S	3.35	3.14	3.92
C <sub>7</sub> + IN GAS	18.74	18.99	21.90
LIQ HC'S	12.93	13.23	13.14

TOTAL	100.00	100.00	100.00
SUB-GROUPING			
C1 -C4	51.22	51.26	48.28
C5 -420 F	42.58	42.07	44.71
420-700 F	5.30	5.60	5.74
700-END PT	0.90	1.07	1.28
C5+ END PT	48.78	48.74	51.72
ISO/NORMAL MOLE RATIO			
C4	0.1303	0.1242	0.1244
C5	0.2215	0.2143	0.2103
C6	0.5153	0.5084	0.4872
C4=	0.0897	0.0907	0.0906
PARAFFIN/OLEFIN RATIO			
C3	0.4749	0.4737	0.4674
C4=	0.3880	0.3894	0.3806
C5	0.5537	0.5568	0.5518
LIQ HC COLLECTION			
PHYS. APPEARANCE	---	CLEAR OIL	CLEAR OIL
DENSITY	---	0.772	0.757
N, REFRACTIVE INDEX	---	1.4332	1.4343
SIMULT'D DISTILATN			
10 WT % @ DEG F	---	292	297
16	---	305	324
50	---	422	439
84	---	617	636
90	---	675	696
RANGE(16-84 %)	---	312	312
WT % @ 420 F	---	49.60	46.60
WT % @ 700 F	---	91.92	90.29

III. RUN 10225-3. Fe/K + UCC-111

Unlike the previous catalyst, this one was formed by physical mixing in the usual way, with UCC-111 as the Molecular Sieve component instead of UCC-109.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C<sub>4</sub>'s are plotted as a function of time on stream in Figs. 23-26. Simulated distillations of the entire pentane+ product from representative samples are shown in Figs. 27-28. Carbon number product distributions are presented in Figs. 29-37. Chromatograms from the simulated distillation of the condensed product of particular samples are shown in Figs. 38-41. Detailed material balances are given in Tables 2A-2C.

As Fig. 23 shows, this catalyst is rather active. Its high WGS activity leads to low hydrogen:carbon monoxide usage ratios; that is, carbon monoxide conversions are higher than hydrogen conversions. Conversion is constant except for the 24 hours between 150 and 174 hours on stream. The constancy of activity both before and after this period suggests that the anomaly was not due to simple catalyst deactivation; the record shows no unusual temperature, pressure or flow during the period of change. The most likely cause is an unnoticed mechanical aberration.

The catalyst also maintained a stable product distribution over the course of the test (Fig. 24). The methane yield of 12

weight percent is consistent with those of promoted iron catalysts tested previously. Combined selectivity to gasoline and diesel oil remained constant at 49 percent, slightly below the average of 55 percent for the other promoted iron catalysts, and similar to the yield from the physical mixture of promoted iron and UCC-104 (Run 10011-10). The latter catalyst produced 39 percent gasoline and 10 percent diesel oil, with 1.7 percent heavies. These differences are probably within the errors of the analysis. The carbon number product distributions (Figs. 29-37) did not show a carbon number cut-off, as was the case with a number of catalysts based on UCC-101. There is a slight curve in the carbon-number distribution plot, as with the catalyst containing UCC-104 (Run 10011-10). This distribution is very like the one produced by a physical mixture of promoted iron and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Run 10011-15). At 280C with a 2:1 hydrogen:carbon monoxide feed, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst produced roughly the same quantity of gasoline and diesel oil as this catalyst. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> did produce slightly more heavies, 4.1 percent compared with 1.7 percent.

The products from these two catalysts are very similar. This catalyst produced approximately 60 percent of the C<sub>4</sub> product as butenes (Fig. 26)--a value comparable to, and actually less than, that produced by the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The pentane from the catalyst is barely isomerized at all (Fig. 25), slightly less than that produced by the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or reference iron catalysts (Run 10011-6). Considering the lower structural isomerization

and degree of unsaturation, the pour point of the condensed product from this UCC-111 catalyst should be higher than that of a comparably heavy product from either reference catalyst. Sample 2 from the Fe/K +  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst has about the same distribution as Sample 12 from this catalyst (Fig. 37). The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> produced a solid product; the product from the UCC-111 is a liquid.

A probable cause of this phenomenon is the position of the double bond in the olefins. The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst produced mostly straight-chain butenes, 96 percent of which were 1-butene. With the UCC-111 catalyst, more than half the straight-chained butenes were cis- and trans-2-butenes. While the Fe/K and UCC-111 catalyst produced very little isomerization of the carbon chain, the position of the double bond was highly isomerized.

The high level of isomerization of the double bond in the n-butenes makes it likely that the double bonds in the higher olefins are also isomerized. This has two beneficial effects on the liquid product. First, the isomerized internal double bonds create kinks in the carbon chains which lower the freezing point of the mixture with a corresponding effect on the pour point; this effect of double bonds is well established in lipid chemistry. Second, the shift of the double bond raises the octane number of the gasoline product. Thus 1-octene has a blending RON of 25; while 3- and 4-octene, with only the double bond shifted, have blending RON's of 85 and 99, respectively.

Since UCC-111 was so poor a catalyst in Task 1, its efficacy

in Task 2, when physically mixed with an active metal component, is remarkable. Its trivial effect on the chemistry of the reaction was anticipated from its low activity. That such innocuous chemistry can have so large an effect on product quality was quite unexpected.



RUN 10225-03

1:1 H<sub>2</sub>:CO  
300 PSIG  
250°C

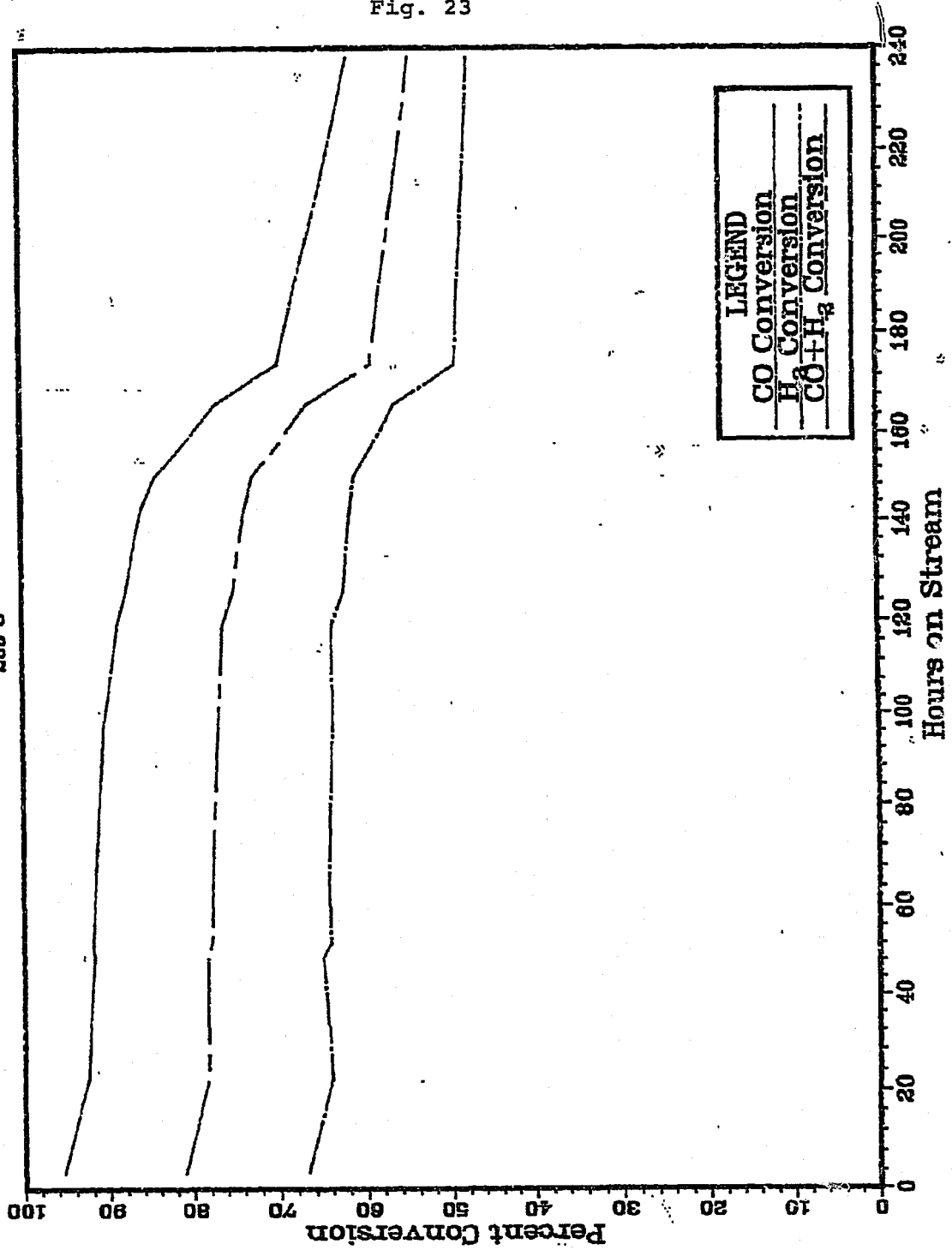


Fig. 23

# RUN 10225-03

1:1 H<sub>2</sub>:CO  
300 PSIG  
250°C

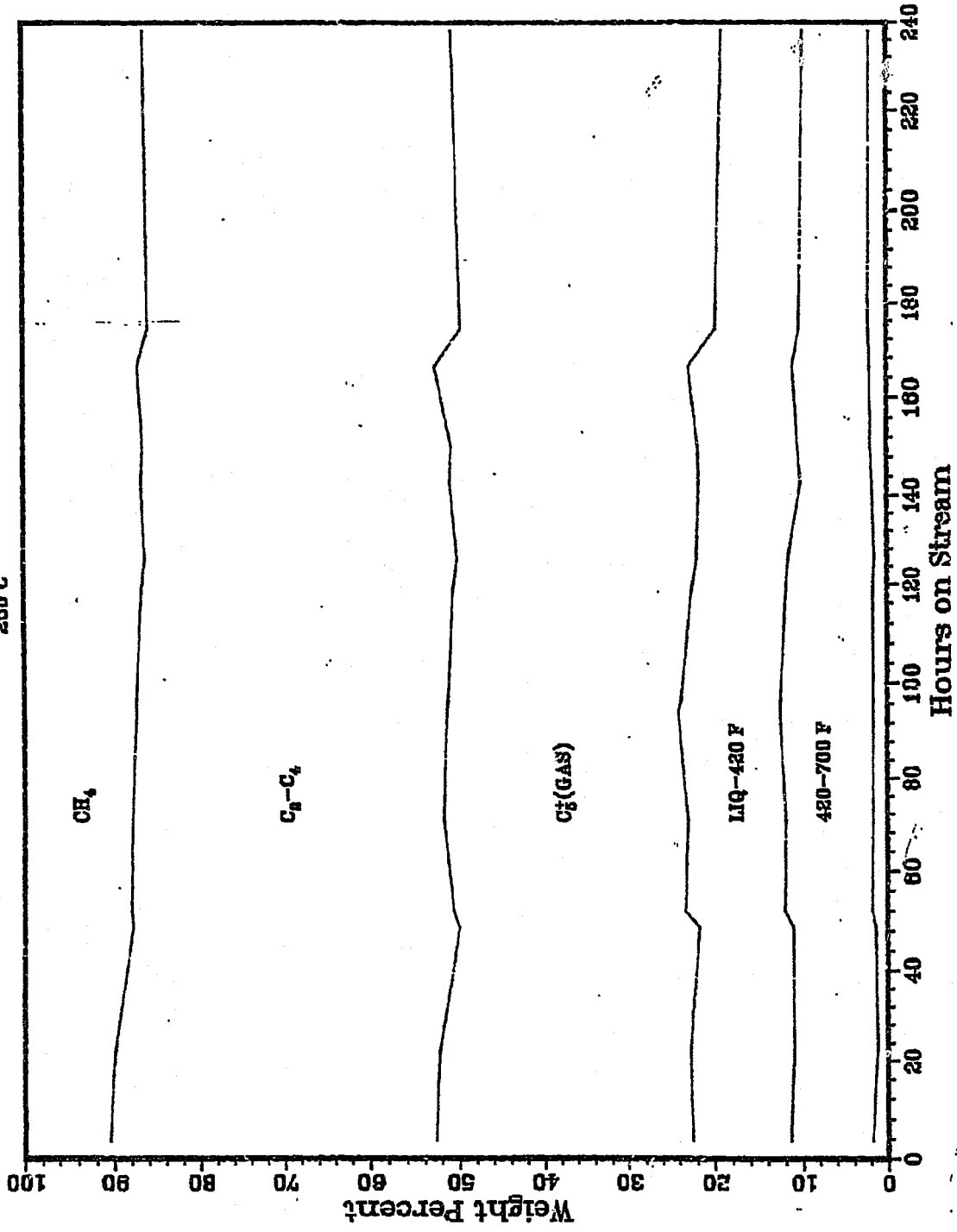


Fig. 24

RUN 10225-03

1M H<sub>2</sub>O  
300 PSIG  
250°C

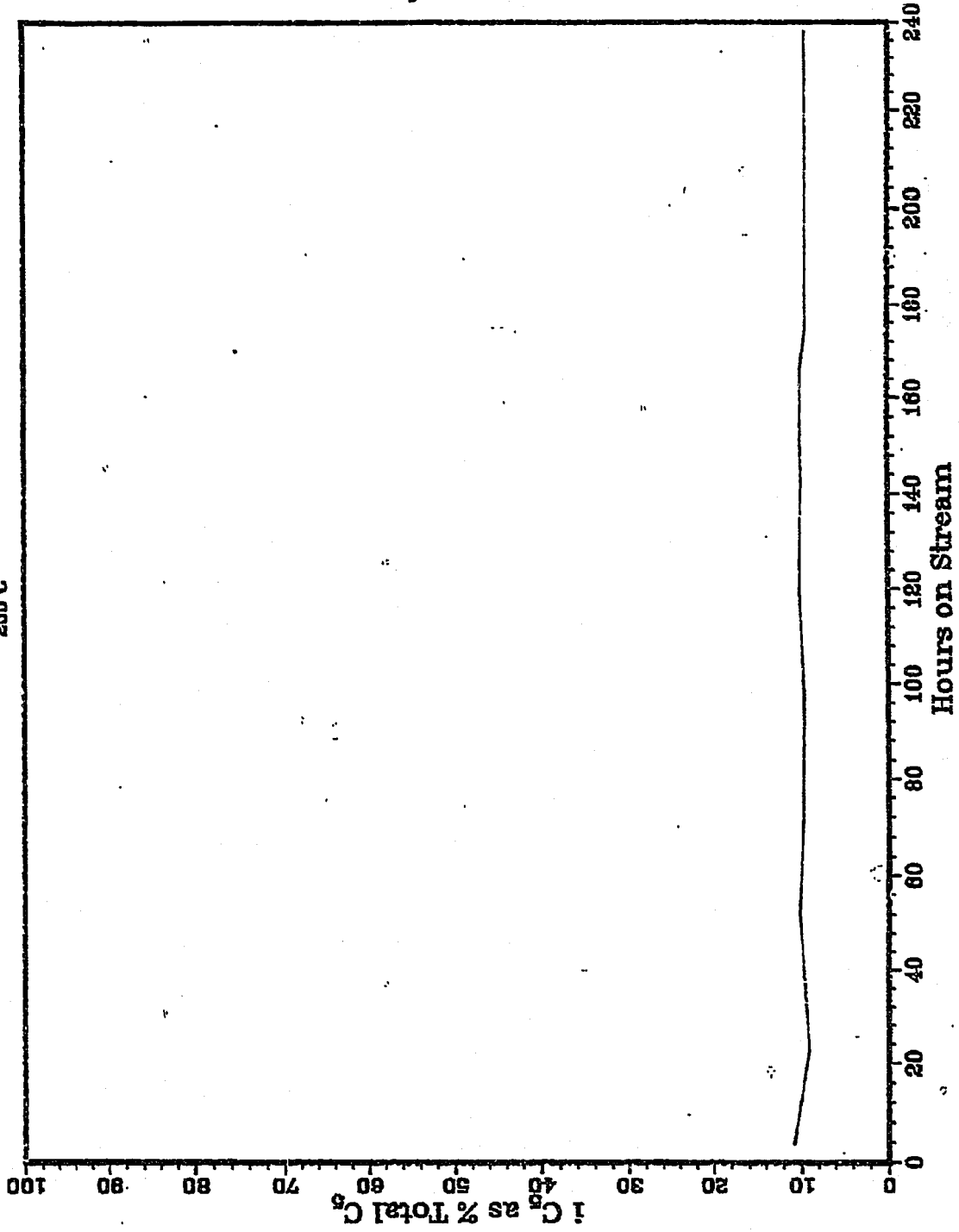


Fig. 25

RUN 10225-03

111E<sub>2</sub>CO  
300 FSIG  
250°C

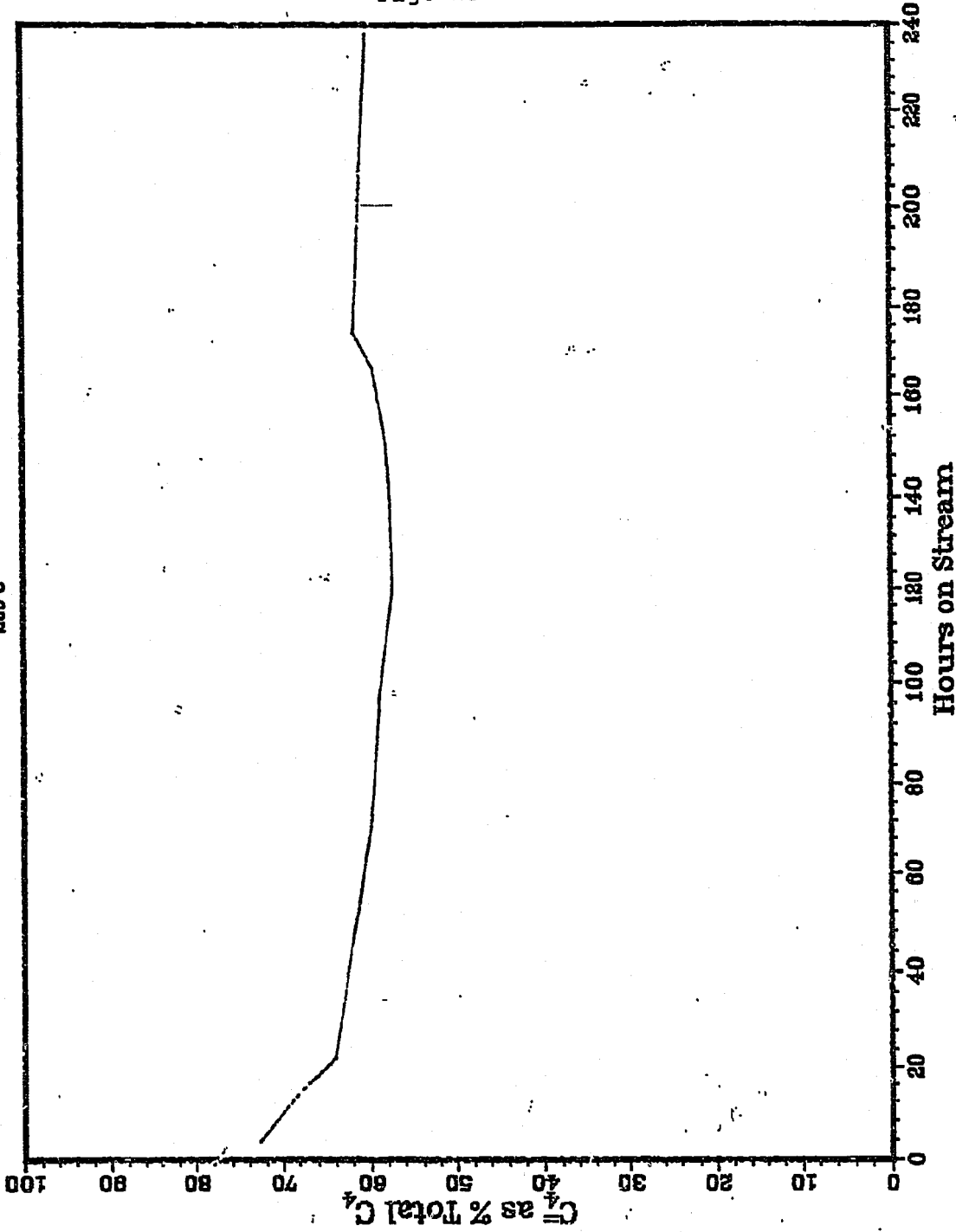


Fig. 26

Fig. 27

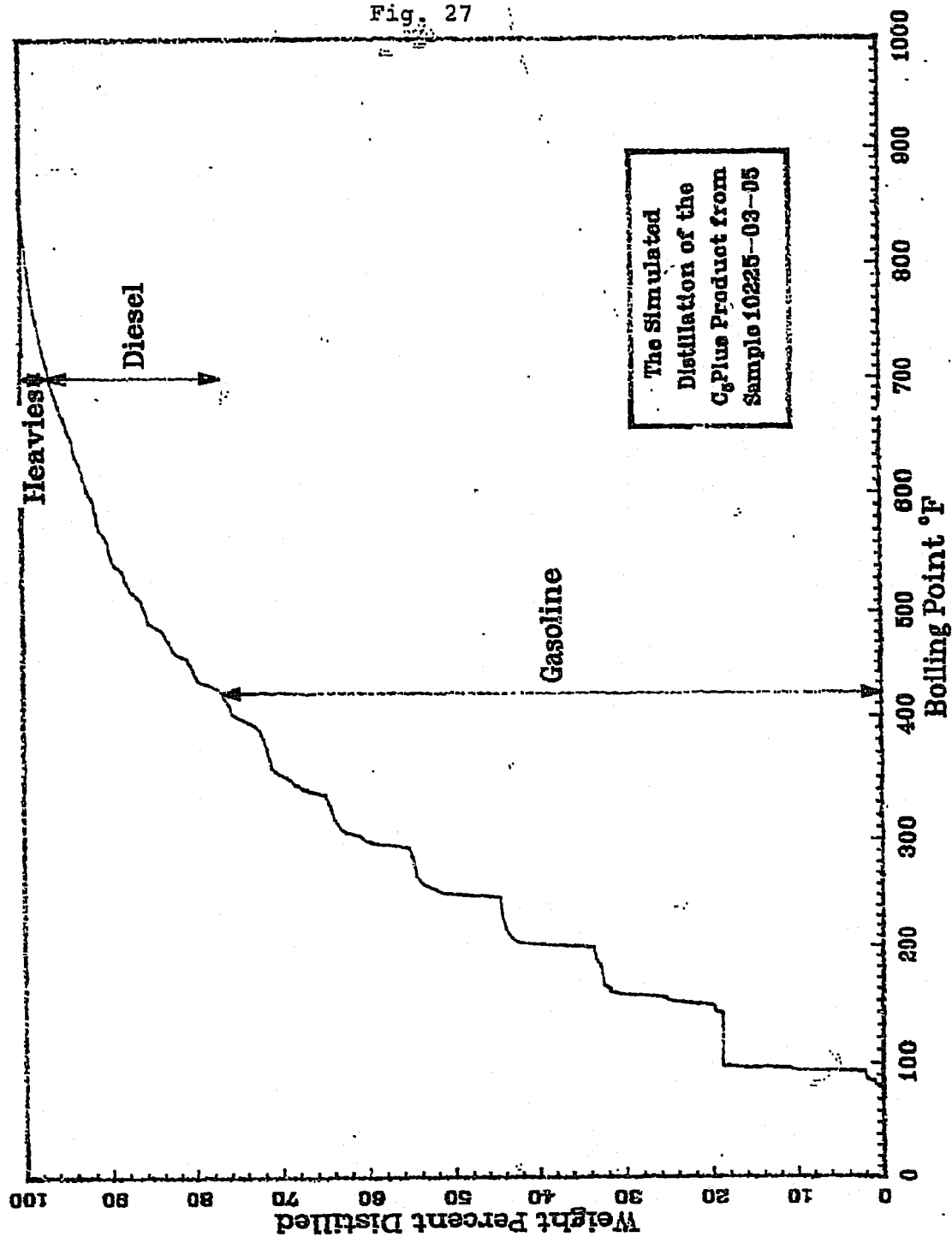


Fig. 28

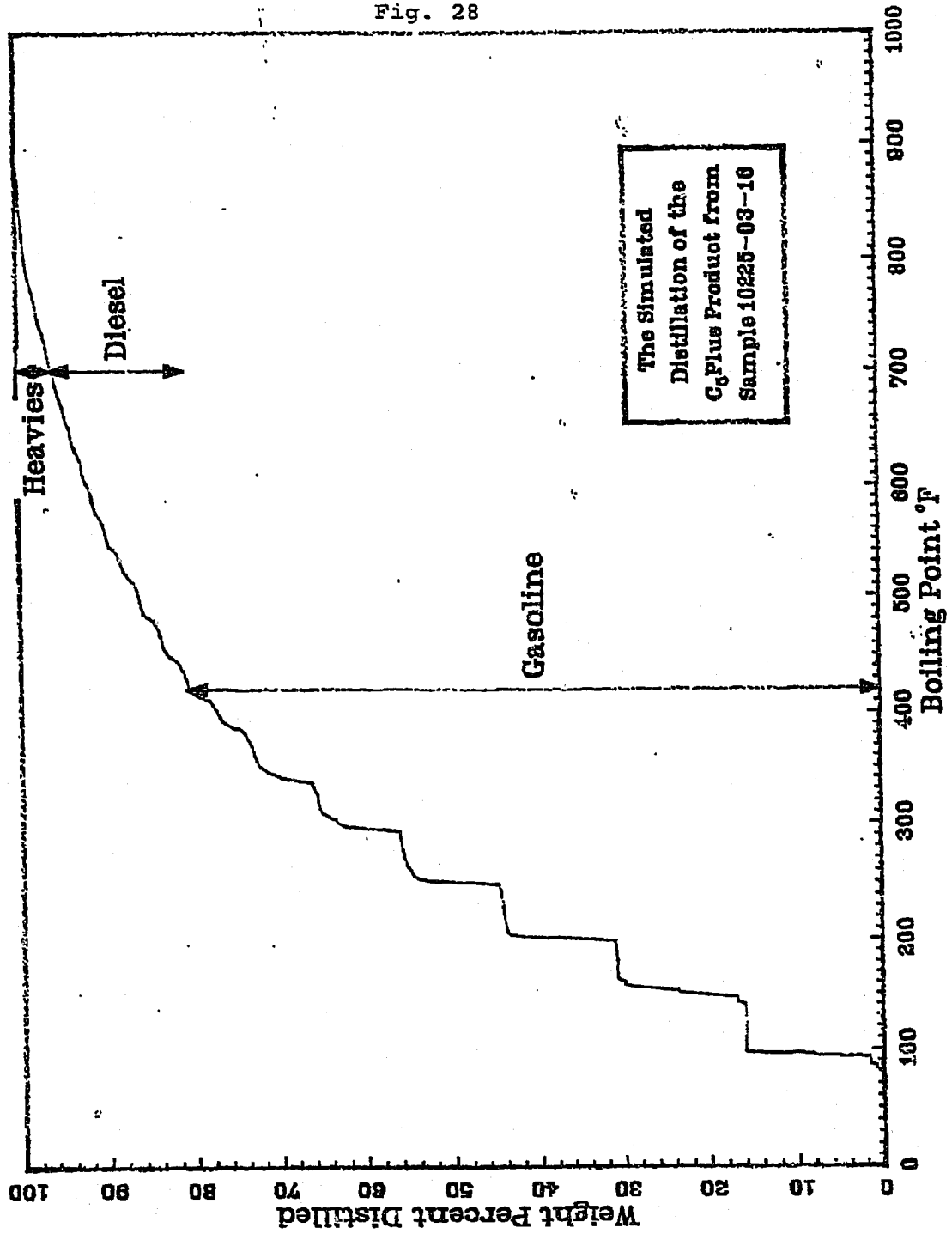


Fig. 29

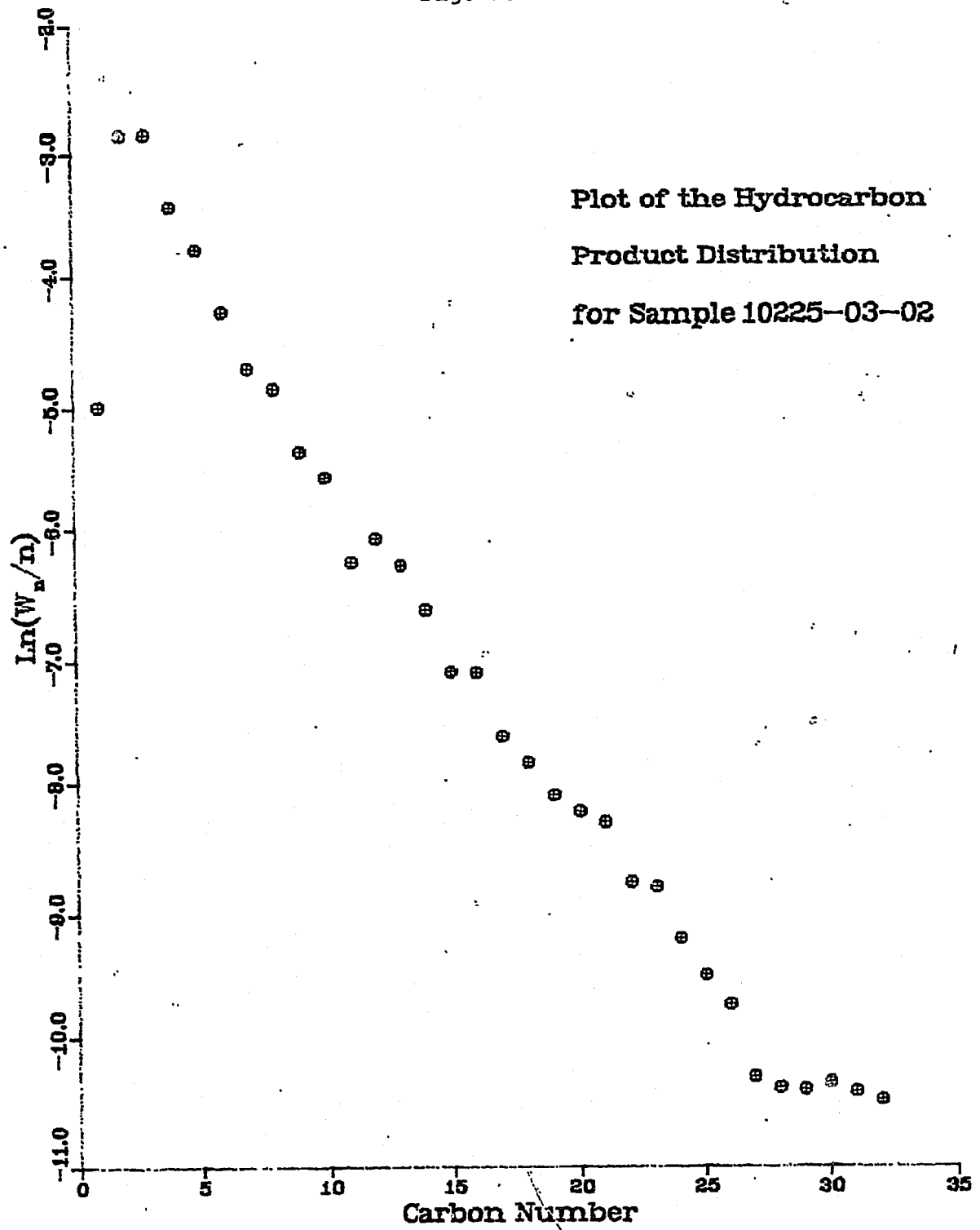


Fig. 30

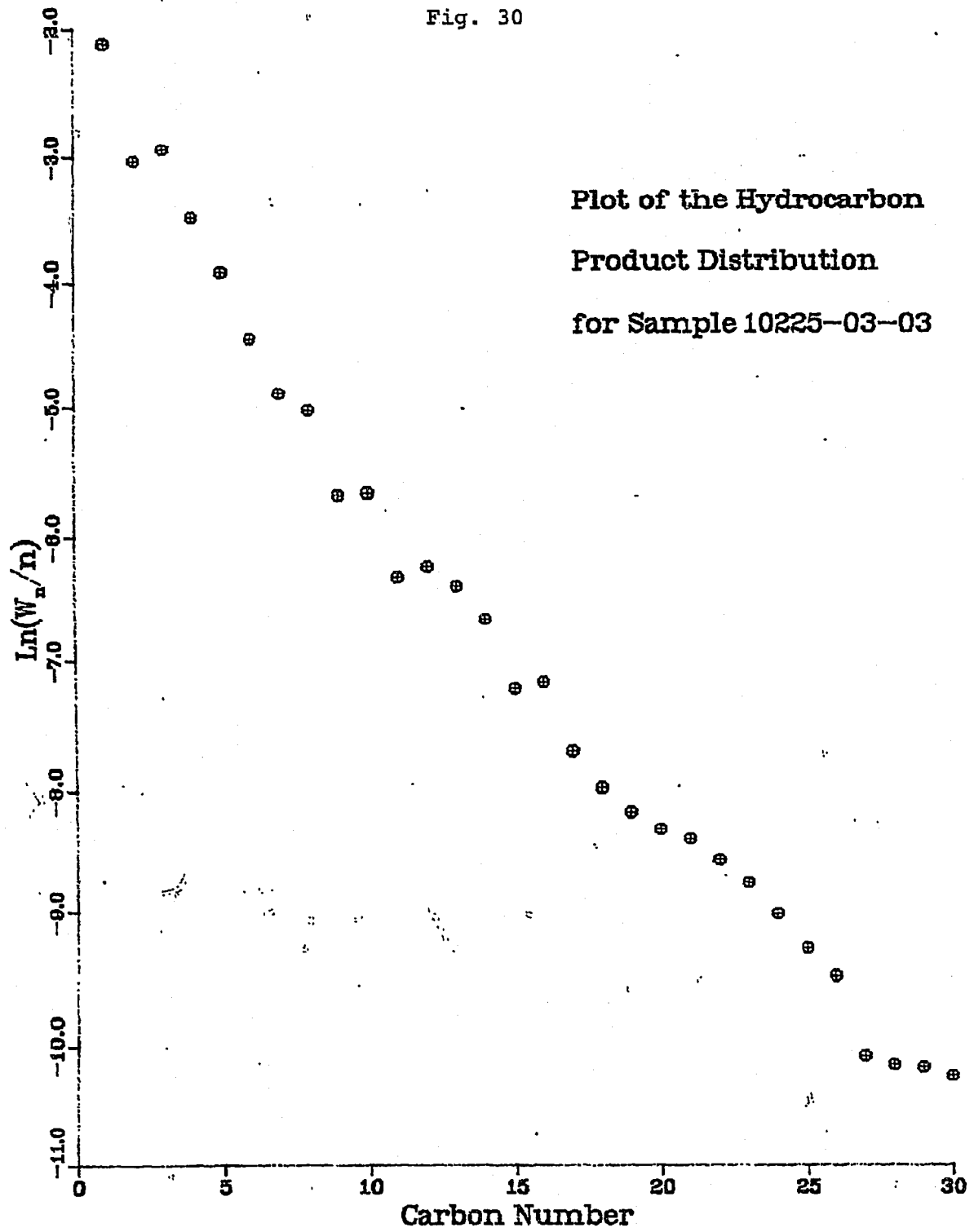




Fig. 31

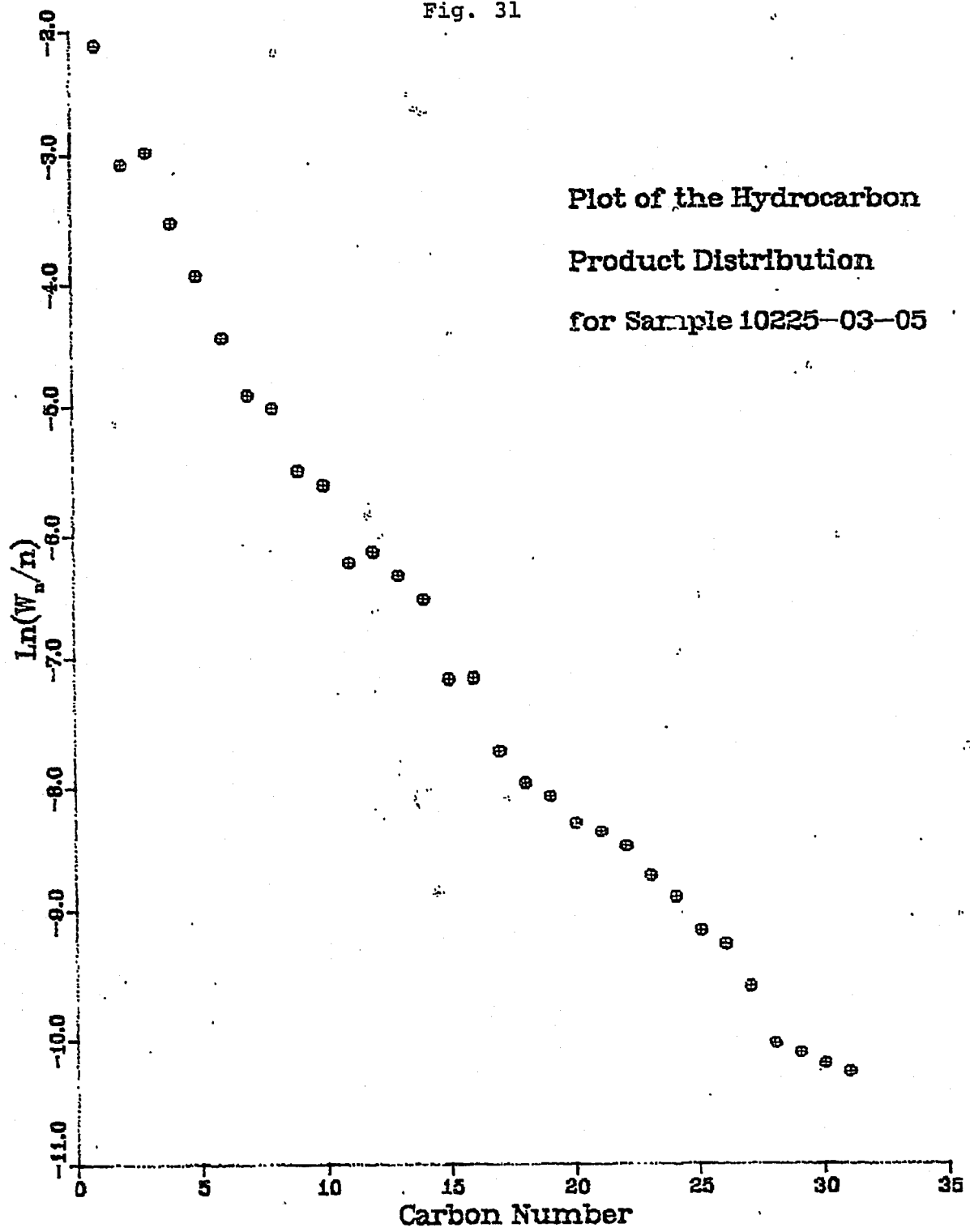


Fig. 32

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-03-07

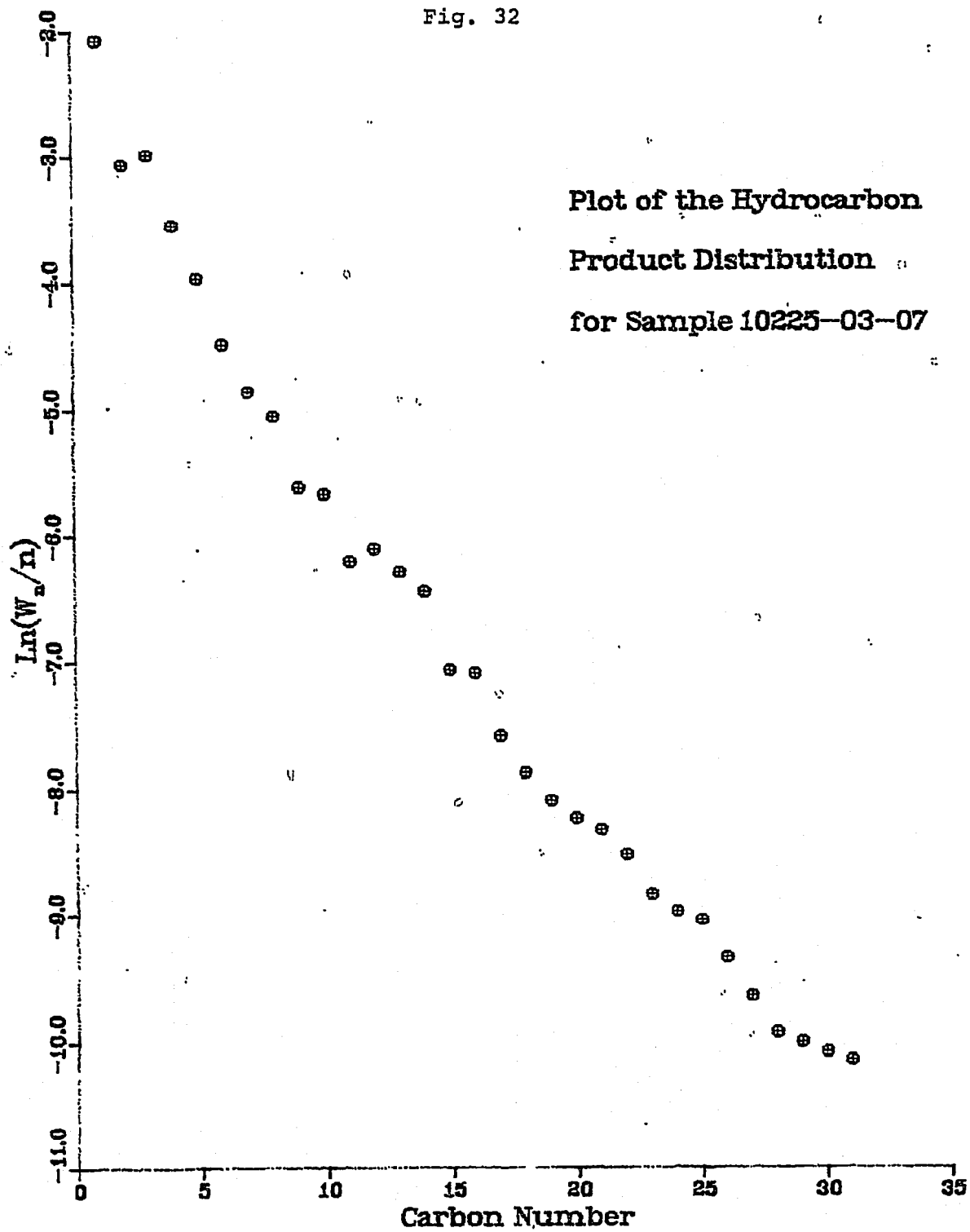


Fig. 33

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-03-10

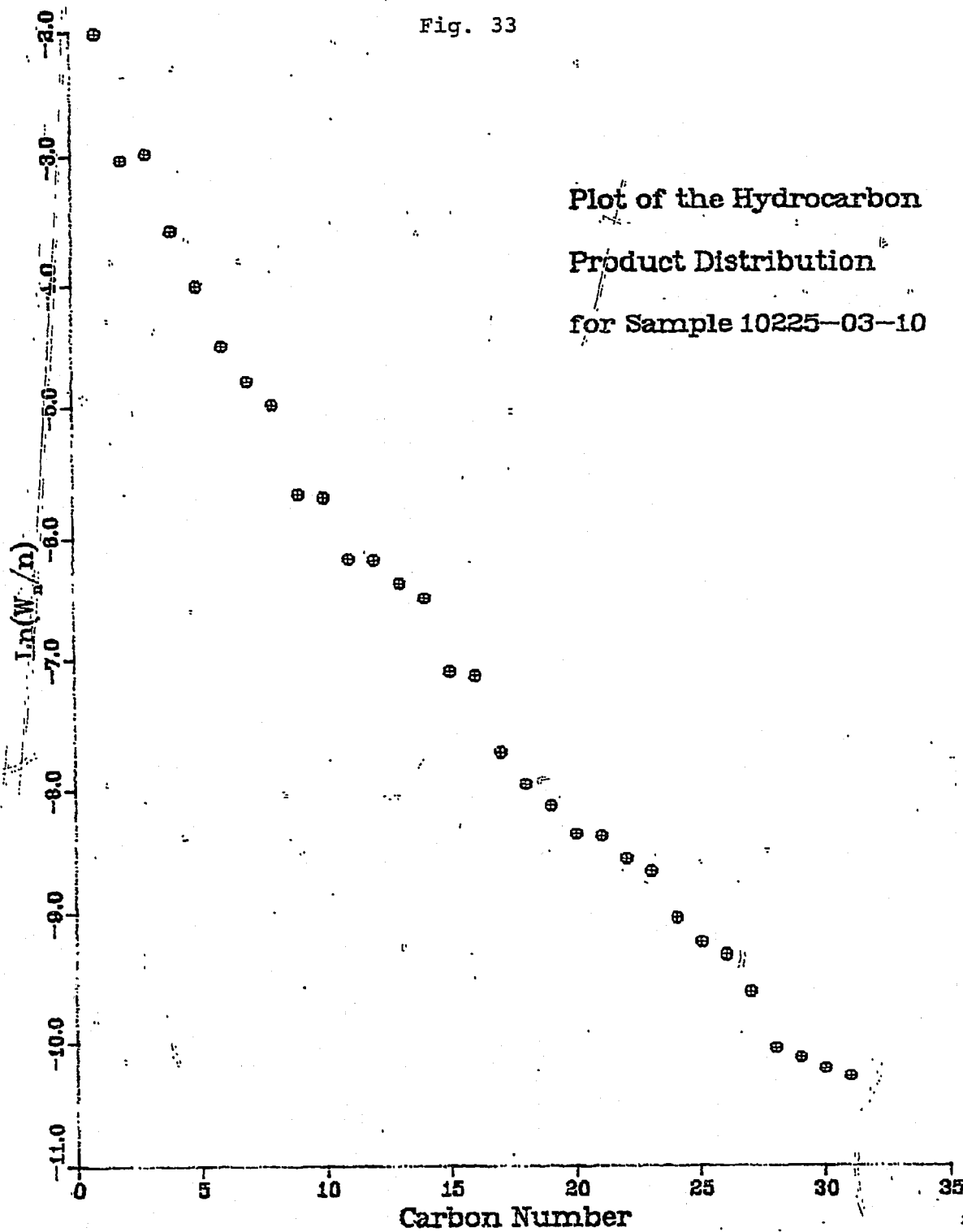


Fig. 34

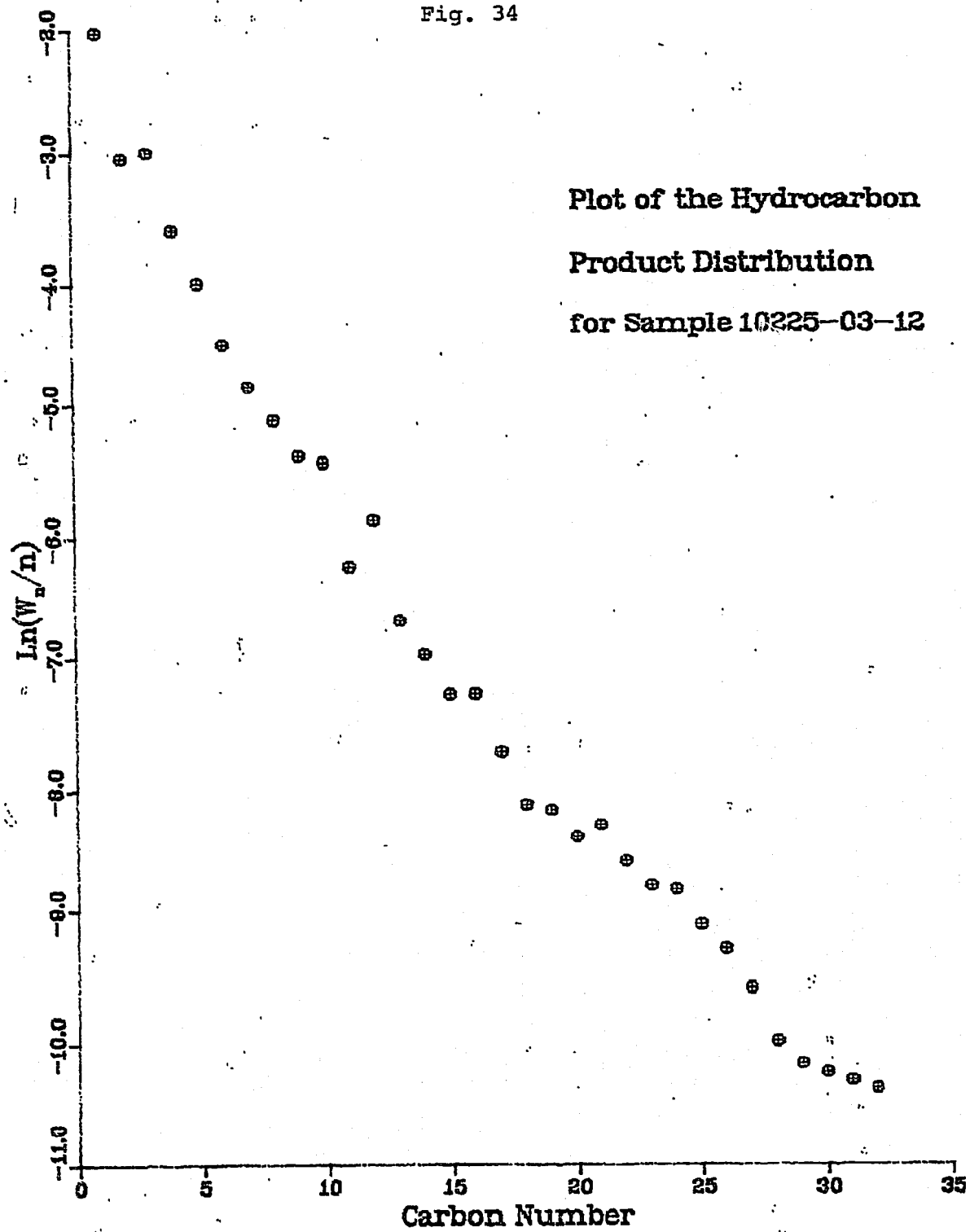


Fig. 35

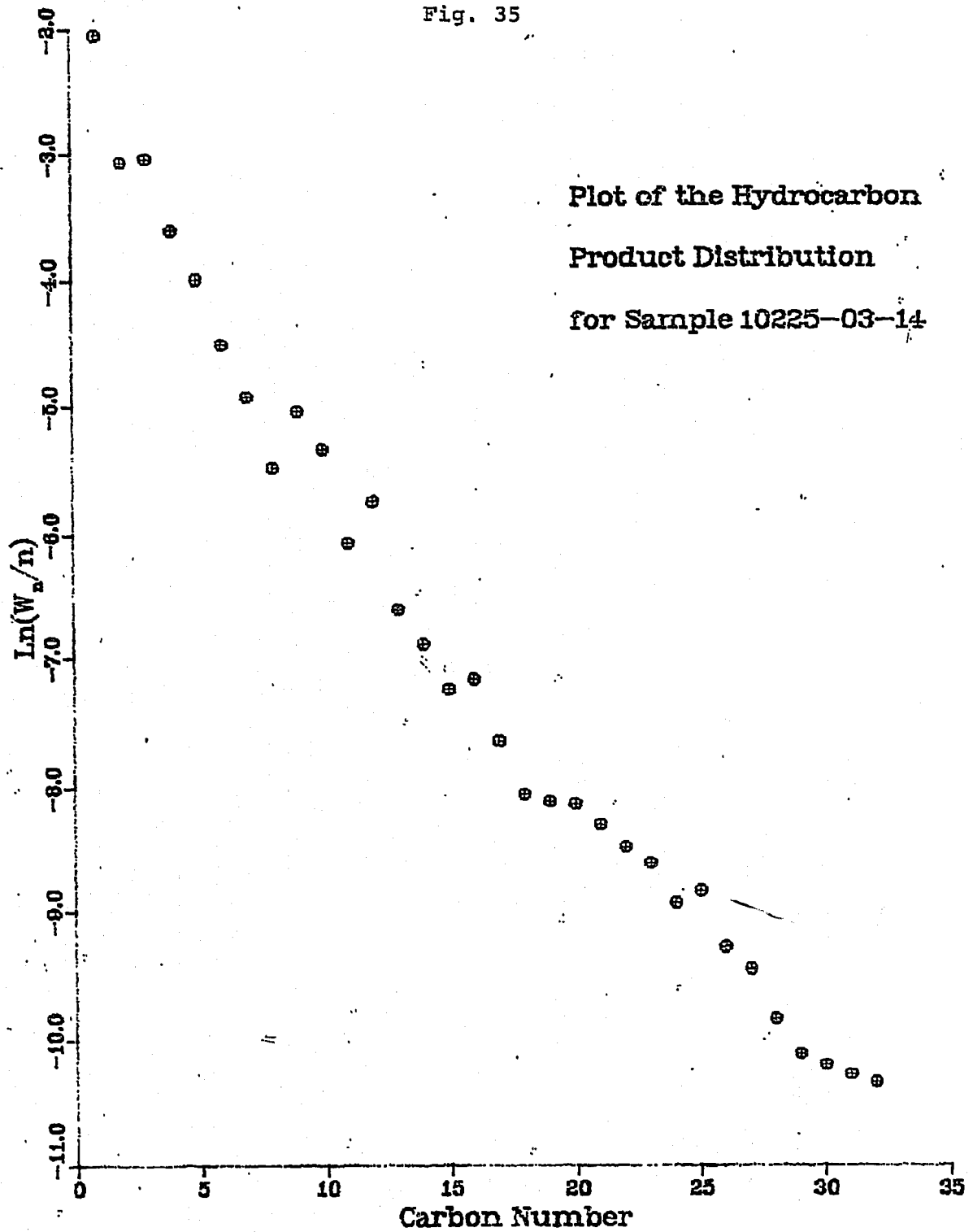


Fig. 36

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-03-16

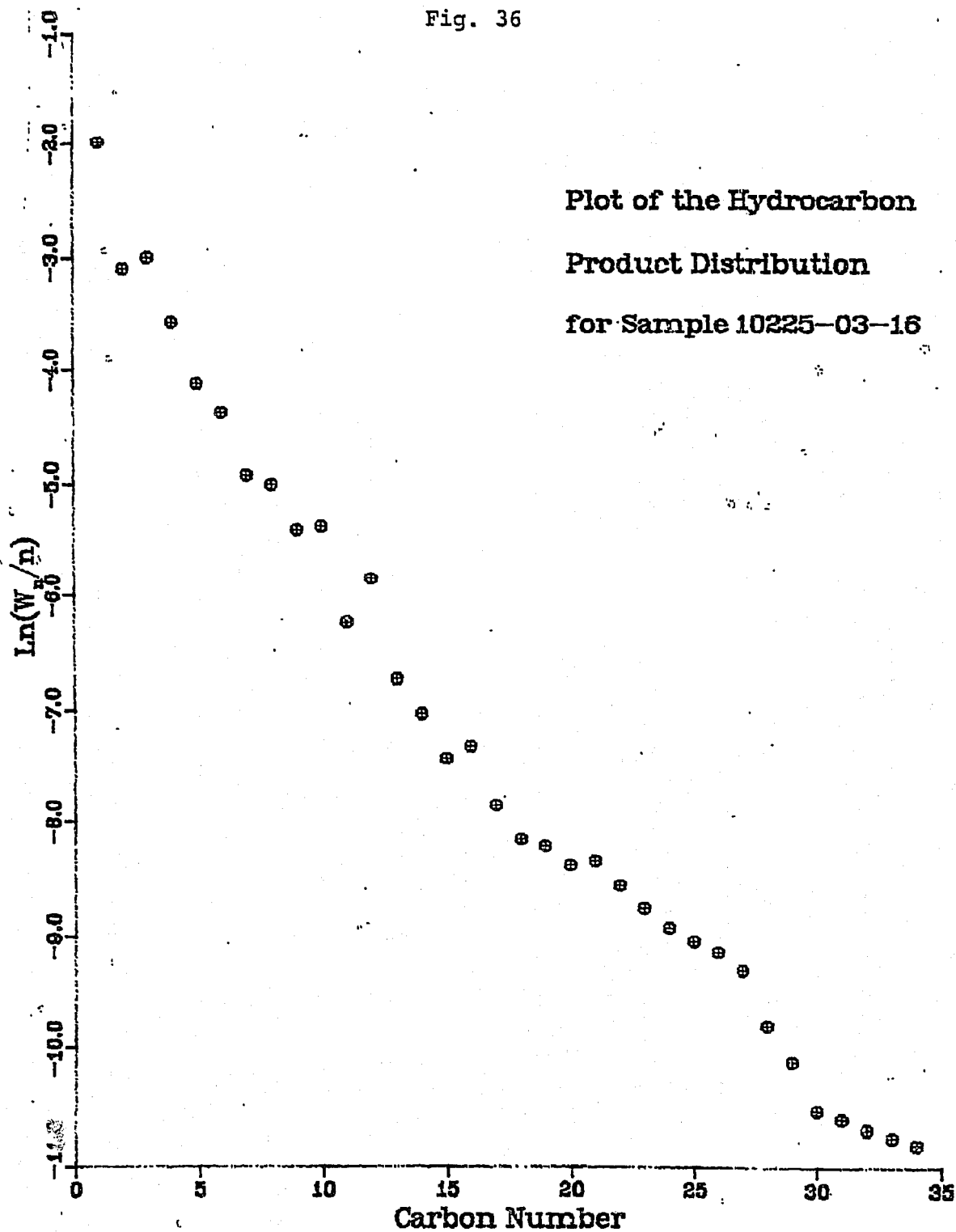
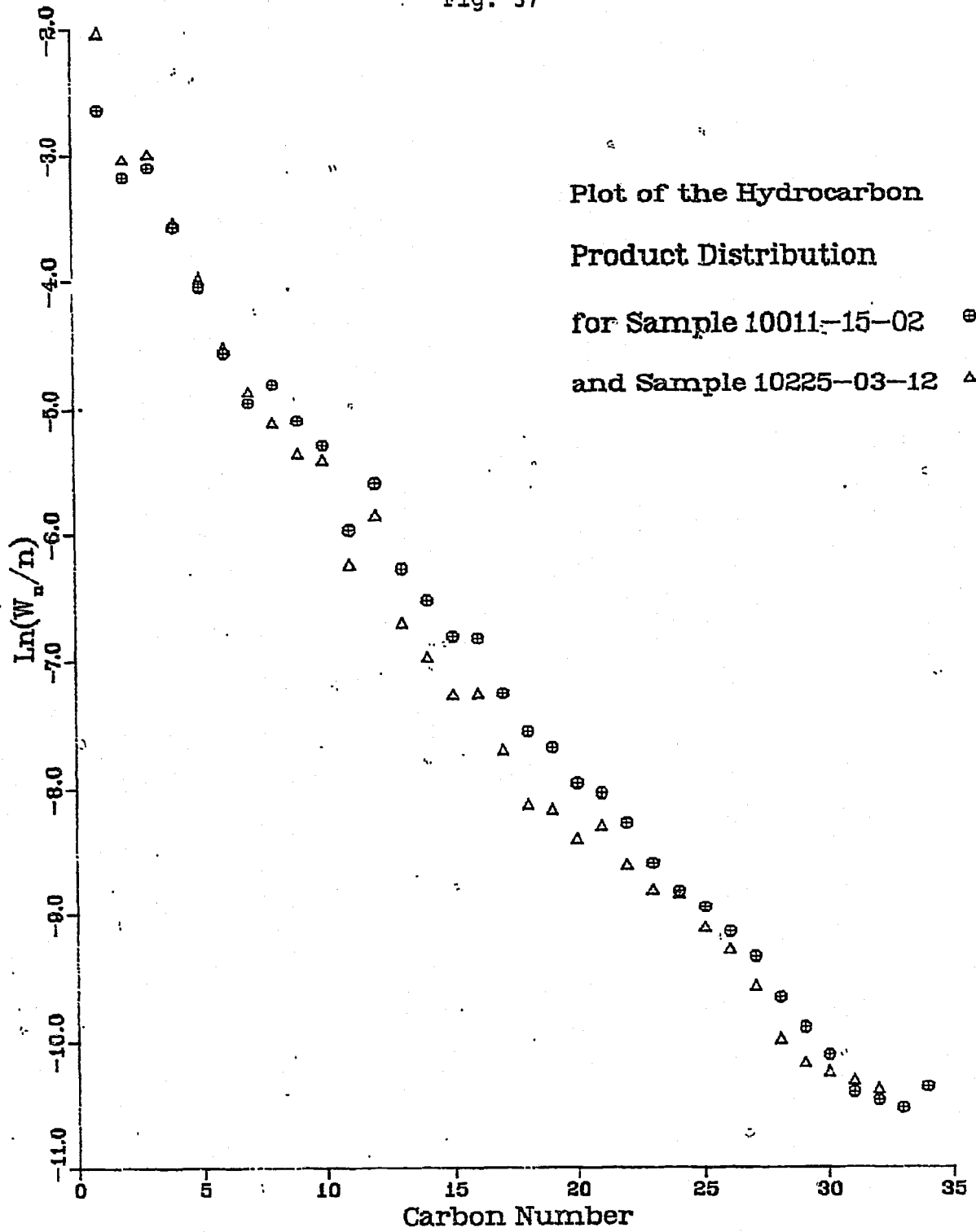
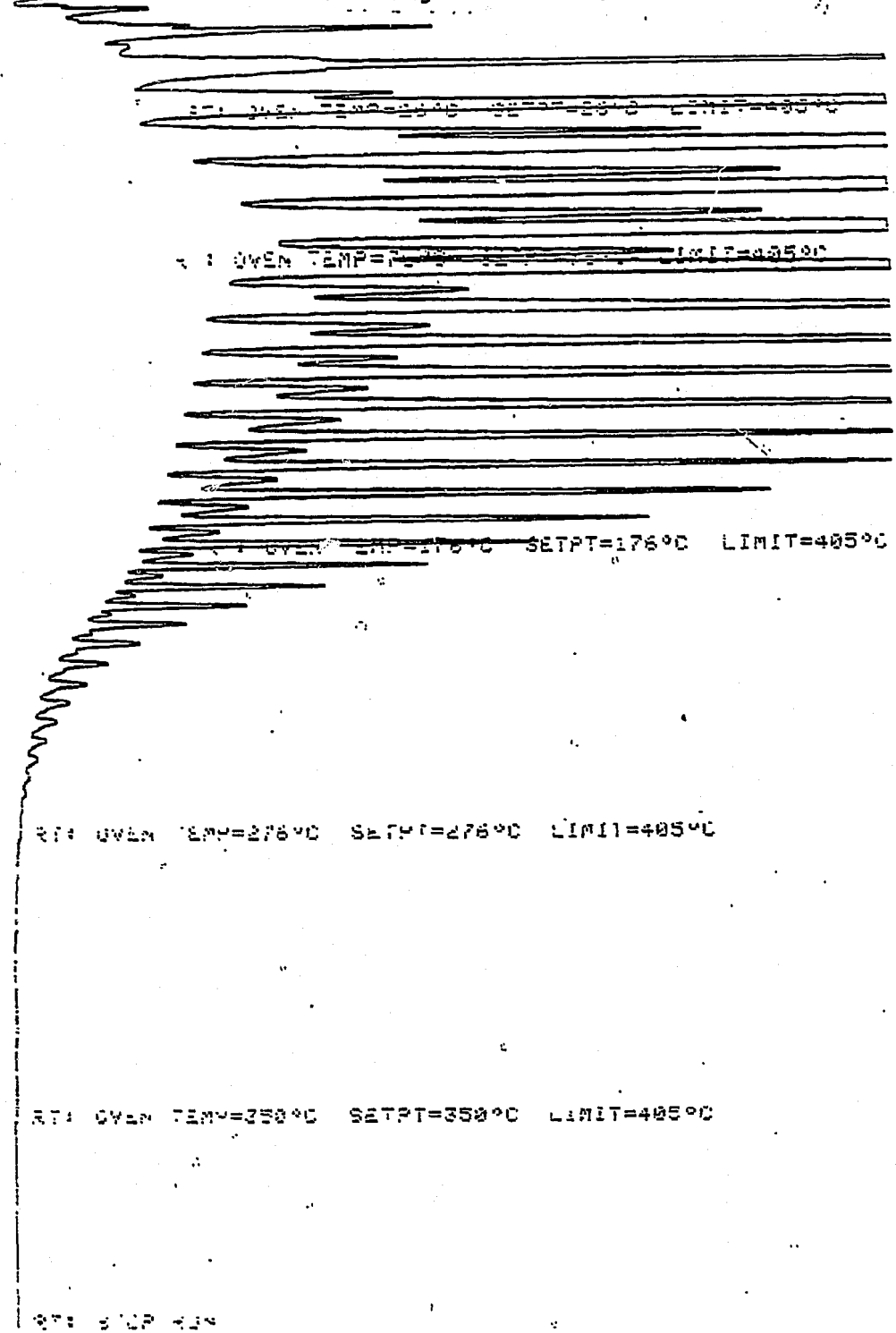


Fig. 37



RTI 31125 8.28

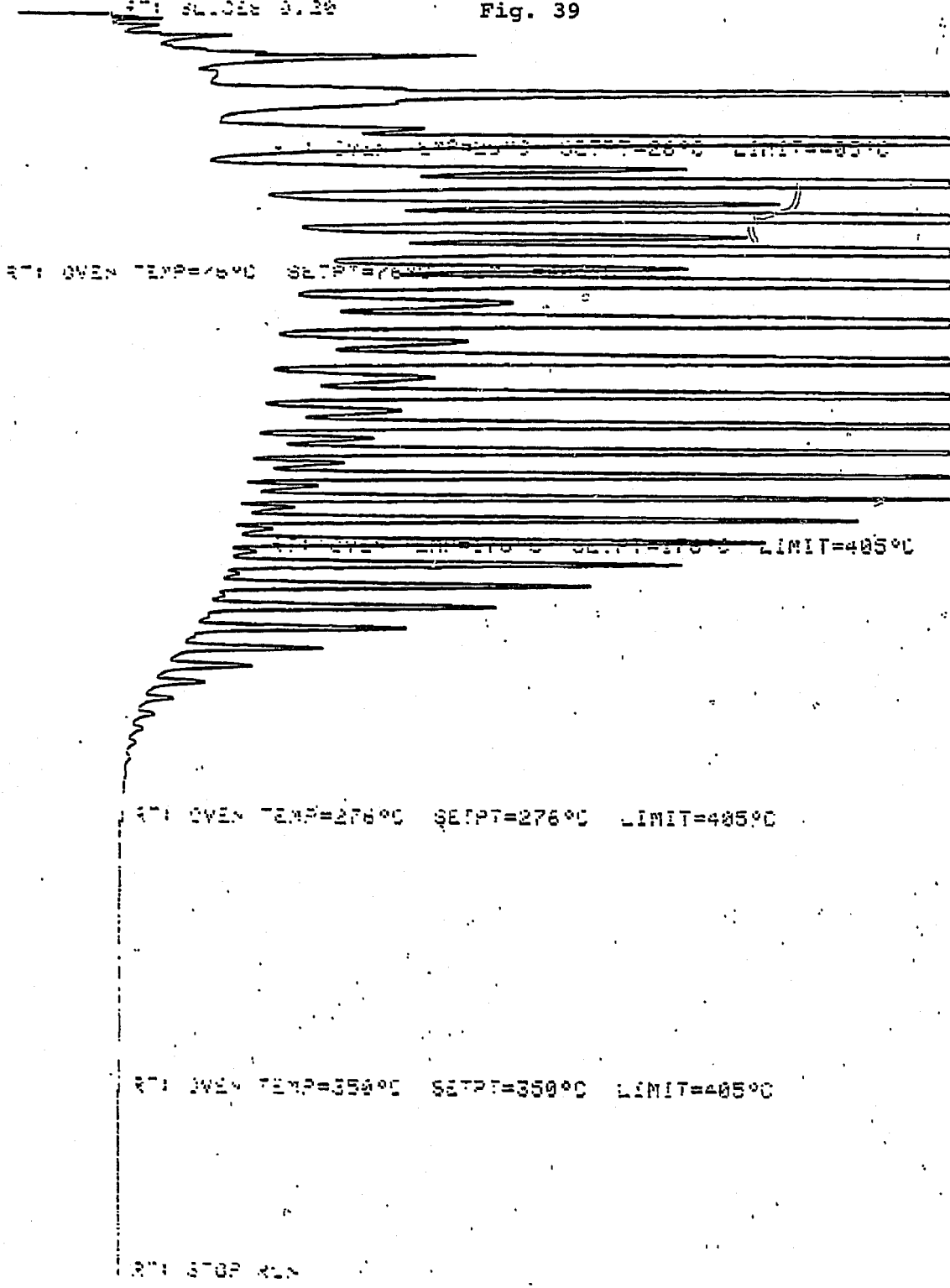
Fig. 38





RT: 21.018 3.20

Fig. 39



SAMP: 1:010225-1-5L

1 1 1111 0.20

Fig. 40

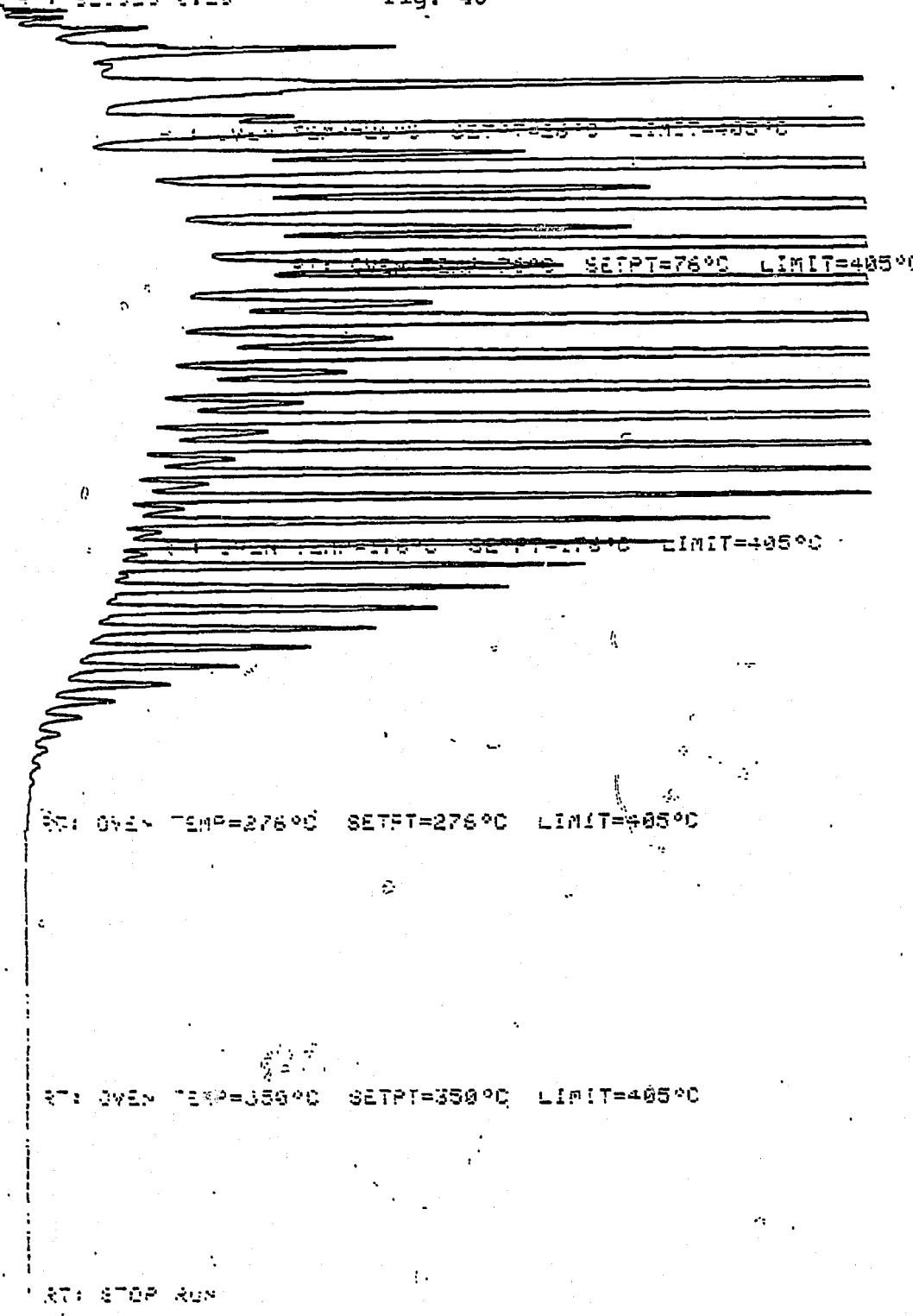


Fig. 41

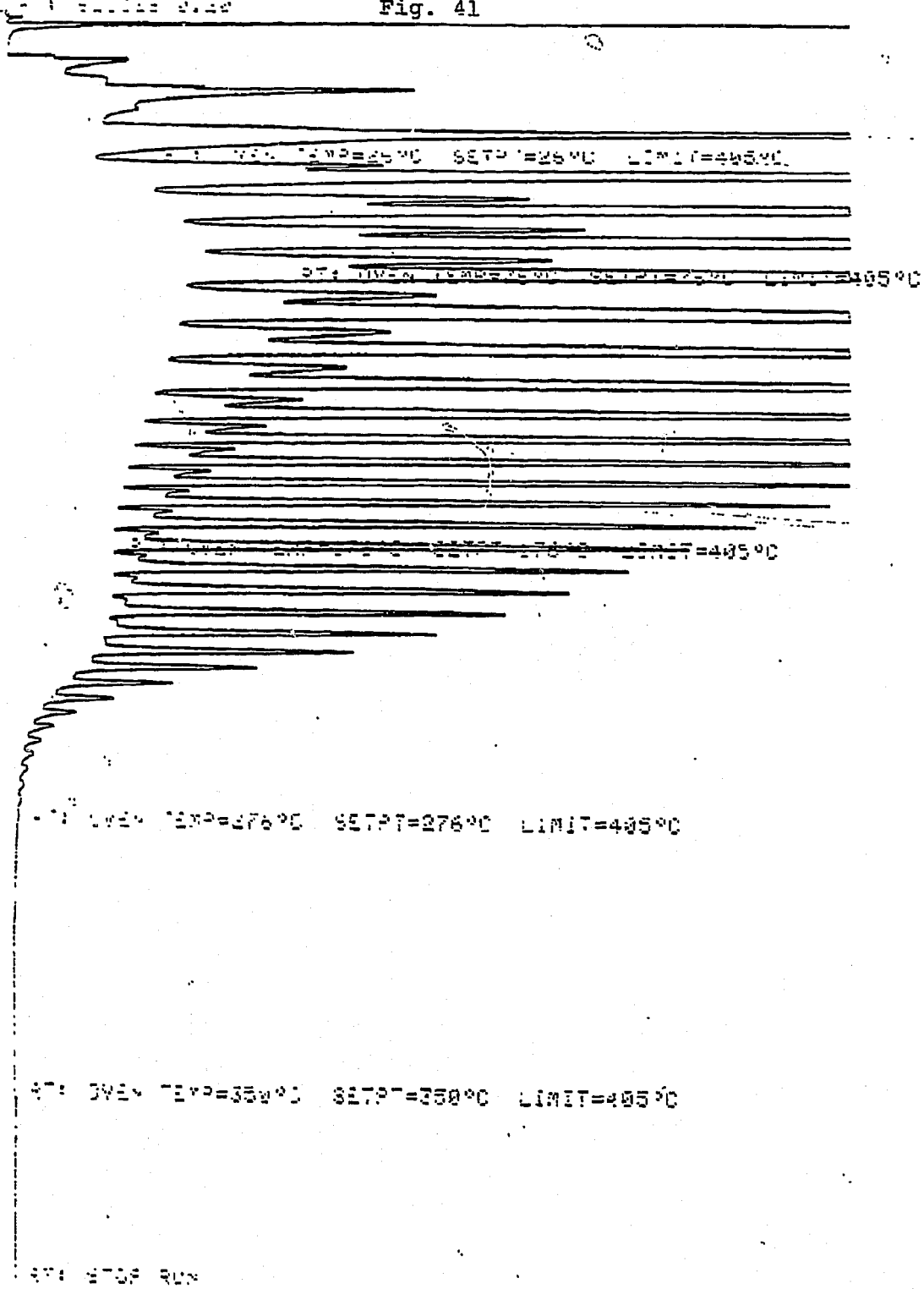


TABLE 2A RESULT OF SYNGAS OPERATION

RUN NO. 10225-03  
 CATALYST FE,K +UCC-111 #10252-3 80 CC 58.6GM (71.1 AFTER RUN +13 G)  
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-03-01	225-03-02	225-03-03	225-03-04	225-03-05
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	3.67	22.33	48.67	51.92	70.58
PRESSURE, PSIG	314	295	296	297	300
TEMP. C	250	250	250	250	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	3.67	22.34	26.33	3.25	21.92
EFFLNT GAS LITER	38.57	259.55	309.35	39.30	266.55
GM AQUEOUS LAYER	2.26	13.78	14.07	1.62	10.90
GM OIL	2.59	15.78	18.80	2.56	17.24
MATERIAL BALANCE					
GM ATOM CARBON %	88.49	92.81	94.47	96.32	97.08
GM ATOM HYDROGEN %	89.08	94.22	97.27	100.85	101.43
GM ATOM OXYGEN %	93.22	100.07	96.97	97.32	97.47
RATIO CHX/(H2O+CO2)	0.9031	0.8575	0.9485	0.9795	0.9918
RATIO X IN CHX	2.3133	2.3641	2.4099	2.4066	2.4085
USAGE H2/CO PRDCT	0.6873	0.6750	0.7201	0.7268	0.7336
RATIO CO2/(H2O+CO2)	0.8242	0.8278	0.8379	0.8451	0.8444
K SHIFT IN EFFLNT	33.46	23.46	22.64	25.28	23.43
CONVERSION					
ON CO %	95.33	92.54	91.80	91.90	91.35
ON H2 %	66.91	64.14	65.12	64.16	64.28
ON CO+H2 %	81.08	78.23	78.27	77.71	77.52
PRDCT SELECTIVITY, WT %:					
CH4	9.44	10.04	12.17	11.97	12.18
C2 HC'S	9.55	10.29	9.65	9.56	9.22
C3H8	4.78	6.88	7.89	7.90	7.94
C3H6=	11.19	8.59	8.15	7.79	7.33
C4H10	3.45	4.36	4.75	4.78	4.77
C4H8=	8.90	7.52	7.40	7.35	6.89
CSH12	3.65	4.47	4.67	4.72	4.71
C5H10=	7.23	5.92	5.31	5.27	5.09
C6H14	2.69	3.54	3.68	3.75	3.84
C6H12= & CYCLO'S	4.52	3.74	3.42	3.35	3.18
C7+ IN GAS	12.01	11.91	11.18	10.32	11.81
LIQ HC'S	22.59	22.74	21.75	23.25	23.03

TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	47.32	47.68	50.00	49.35	48.34
C5 -420 F	41.16	41.23	38.81	38.56	39.65
420-700 F	9.71	9.85	9.74	10.23	10.23
700-END PT	1.81	1.24	1.44	1.86	1.78
C5+-END PT	52.68	52.32	50.00	50.65	51.66
ISO/NORMAL MOLE RATIO					
C4	0.0845	0.0589	0.0541	0.0518	0.0505
C5	0.1217	0.1006	0.1116	0.1143	0.1085
C6	0.1897	0.1615	0.1461	0.1476	0.1423
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	0.4074	0.7644	0.9238	0.9680	1.0338
C4	0.3744	0.5598	0.6190	0.6287	0.6678
C5	0.4903	0.7346	0.8545	0.8711	0.8995
LIQ HC COLLECTION					
PHYS. APPEARANCE		LT YL OIL	CLR OIL		CLR OIL
DENSITY	-	0.753	0.753	-	0.753
N, REFRACTIVE INDEX	-	1.4244	1.4232	-	1.4232
SIMULT'D DISTILATN					
10 WT % @ DEG F		256	257		258
16		287	297		299
50		414	425		426
84		587	602		612
90		646	663		674
RANGE(16-84 %)		300	305		313
WT % @ 420 F		51.25	48.57		47.83
WT % @ 700 F		94.54	93.36		92.27

TABLE 2B RESULT OF SYNGAS OPERATION

RUN NO. 10225-03  
 CATALYST FE,K +UCC-111 #10252-3 80 CC 58.6GM (71.1 AFTER RUN +13 G)  
 FEED H<sub>2</sub>:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-03-07	225-03-08	225-03-10	225-03-11
FEED H <sub>2</sub> :CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	94.42	96.58	118.58	125.58
PRESSURE,PSIG	297	289	299	289
TEMP. C	250	251	250	250
FEED CC/MIN	400	400	400	400
HOURS FEEDING	23.83	2.17	24.17	7.00
EFFLNT GAS LITER	293.18	25.52	309.42	89.96
GM AQUEOUS LAYER	11.44	1.01	11.26	3.19
GM OIL	19.52	1.67	18.60	5.01
MATERIAL BALANCE				
GM ATOM CARBON %	97.33	92.86	100.88	98.79
GM ATOM HYDROGEN %	101.91	97.31	102.26	100.49
GM ATOM OXYGEN %	97.45	93.23	102.54	101.67
RATIO CHX/(H <sub>2</sub> O+CO <sub>2</sub> )	0.9976	0.9918	0.9663	0.9404
RATIO X IN CHX	2.4203	2.4221	2.4381	2.4467
USAGE H <sub>2</sub> /CO PRDCT	0.7375	0.7366	0.7219	0.7126
RATIO CO <sub>2</sub> /(H <sub>2</sub> O+CO <sub>2</sub> )	0.8464	0.8450	0.8526	0.8520
K SHIFT IN EFFLNT	22.09	21.86	19.04	17.90
CONVERSION				
ON CO %	90.55	90.53	88.87	87.72
ON H <sub>2</sub> %	63.83	63.78	63.88	62.47
ON CO+H <sub>2</sub> %	76.88	76.85	76.29	74.99
PRDCT SELECTIVITY,WT %				
CH <sub>4</sub>	12.67	12.73	13.38	13.78
C <sub>2</sub> HC'S	9.33	9.37	9.67	9.86
C <sub>3</sub> H <sub>8</sub>	8.23	8.27	8.51	8.48
C <sub>3</sub> H <sub>6</sub> =	6.97	7.00	6.83	6.86
C <sub>4</sub> H <sub>10</sub>	4.82	4.84	4.81	4.80
C <sub>4</sub> H <sub>8</sub> =	6.68	6.70	6.26	6.25
C <sub>5</sub> H <sub>12</sub>	4.65	4.67	4.51	4.48
C <sub>5</sub> H <sub>10</sub> =	4.86	4.88	4.61	4.55
C <sub>6</sub> H <sub>14</sub>	3.65	3.66	3.64	3.59
C <sub>6</sub> H <sub>12</sub> = & CYCLO'S	3.03	3.04	2.98	2.95
C <sub>7</sub> + IN GAS	11.04	11.08	12.17	12.37
LIQ HC'S	24.07	23.76	22.62	22.02

TOTAL	100.00	100.00	100.00	100.00
SUB-GROUPING				
C1 -C4	48.70	48.90	49.48	50.03
C5 -420 F	38.59	38.50	38.58	38.30
420-700 F	11.05	10.93	10.25	10.13
700-END PT	1.66	1.66	1.70	1.54
C5+-END PT	51.30	51.10	50.52	49.97
ISO/NORMAL MOLE RATIO				
C4	0.0486	0.0486	0.0493	0.0505
C5	0.1061	0.1061	0.1126	0.1129
C6	0.1372	0.1372	0.1455	0.1359
C4=	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO				
C3	1.1265	1.1265	1.1883	1.1806
C4	0.6963	0.6963	0.7411	0.7415
C5	0.9309	0.9309	0.9501	0.9570
LIQ HC COLLECTION				
PHYS. APPEARANCE	CLR OIL		CLR OIL	
DENSITY	0.753	-	0.755	-
N, REFRACTIVE INDEX	1.4228	-	1.4226	-
SIMULT'D DISTILATN				
10 WT % @ DEG F	258		258	
16	300		301	
50	428		429	
84	602		604	
90	667		672	
RANGE(16-84 %)	302		303	
WT % @ 420 F	47.20		47.17	
WT % @ 700 F	93.12		92.50	

TABLE 2C RESULT OF SYNGAS OPERATION

RUN NO. 10225-03  
 CATALYST FE,K +UCC-111 #10252-3 80 CC 58.6GM (71.1 AFTER RUN +13 G)  
 FEED H2:CO:ARGON OF 50:50: 0 @ 400 CC/MN OR 300 GHSV

RUN & SAMPLE NO.	10225-03-12	225-03-13	225-03-14	225-03-15	225-03-16
	=====	=====	=====	=====	=====
FEED H2:CO:AR	50:50: 0	50:50: 0	50:50: 0	50:50: 0	50:50: 0
HRS ON STREAM	142.58	150.08	166.08	174.08	238.08
PRESSURE, PSIG	299	298	298	291	298
TEMP. C	250	250	250	250	250
FEED CC/MIN	400	400	400	400	400
HOURS FEEDING	24.00	7.50	23.50	8.00	72.00
EFFLNT GAS LITER	316.90	93.79	320.95	113.80	1149.80
GM AQUEOUS LAYER	10.92	3.40	10.64	3.40	30.58
GM OIL	17.18	4.95	15.51	3.75	33.76
MATERIAL BALANCE					
GM ATOM CARBON %	100.49	94.29	96.69	90.11	99.89
GM ATOM HYDROGEN %	103.02	95.89	99.55	96.38	103.69
GM ATOM OXYGEN %	101.56	96.10	97.30	93.54	99.67
RATIO CHX/(H2O+CO2)	0.9774	0.9588	0.9851	0.9063	1.0065
RATIO X IN CHX	2.4358	2.4378	2.4157	2.4408	2.4326
USAGE H2/CO PRDCT	0.7313	0.7306	0.7523	0.7369	0.8024
RATIO CO2/(H2O+CO2)	0.8475	0.8397	0.8236	0.8081	0.7874
K SHIFT IN EFFLNT	15.41	13.04	9.07	7.52	5.26
CONVERSION					
ON CO %	85.80	84.12	76.90	69.66	61.70
ON H2 %	61.59	61.12	56.42	49.31	47.61
ON CO+H2 %	73.55	72.52	66.51	59.14	54.53
PRDCT SELECTIVITY, WT %					
CH4	13.36	13.56	12.98	14.10	13.72
C2 HC'S	9.62	9.62	9.30	9.61	9.14
C3H8	8.28	8.20	7.40	7.57	7.75
C3H6=	6.85	6.88	6.98	7.56	7.30
C4H10	4.77	4.73	4.43	4.52	4.66
C4H8=	6.30	6.34	6.34	7.04	6.84
C5H12	4.54	4.45	4.33	4.33	4.32
C5H10=	4.80	4.76	4.96	5.05	3.76
C6H14	3.74	3.58	3.54	3.52	3.61
C6H12= & CYCLO'S	3.09	3.03	3.18	3.38	3.88
C7+ IN GAS	12.96	13.01	13.72	13.55	16.05
LIQ HC'S	21.70	21.85	22.85	19.77	18.99



TOTAL	100.00	100.00	100.00	100.00	100.00
SUB-GROUPING					
C1 -C4	49.18	49.32	47.43	50.40	49.40
C5 -420 F	40.67	40.19	41.55	39.32	40.76
420-700 F	8.42	8.52	9.04	8.11	7.78
700-END PT	1.74	1.97	1.99	2.18	2.05
C5+-END PT	50.82	50.68	52.57	49.60	50.60
ISO/NORMAL MOLE RATIO					
C4	0.0485	0.0504	0.0524	0.0558	0.0482
C5	0.1110	0.1122	0.1121	0.1040	0.1053
C6	0.1421	0.1330	0.1326	0.1361	0.1376
C4=	0.0000	0.0000	0.0000	0.0000	0.0000
PARAFFIN/OLEFIN RATIO					
C3	1.1538	1.1365	1.0108	0.9559	1.0131
C4	0.7302	0.7205	0.6739	0.6200	0.6568
C5	0.9192	0.9088	0.8472	0.8343	1.1171
LIQ HC COLLECTION					
PHYS. APPEARANCE	CLR OIL		CLR OIL		MLKY OIL
DENSITY	0.759	-	0.754	-	0.762
N, REFRACTIVE INDEX	1.4231		1.4239		1.4261
SIMULT'D DISTILATN					
10 WT % @ DEG F	262		268		300
16	301		305		313
50	414		416		436
84	621		627		652
90	677		683		709
RANGE(16-84 %)	320		322		339
WT % @ 420 F	53.22		51.75		48.18
WT % @ 700 F	92.00		91.30		89.18

#### IV. RUN 10225-1, Fe/K on LZ-105-6

This catalyst was prepared by ammoniacal precipitation of  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$  from a slurry of  $\text{Fe}(\text{NO}_3)_3$  and LZ105-6, a Union Carbide Molecular Sieve with a structure similar to that of Mobil Oil's ZSM-5. This metal-loaded powder, containing 20 percent iron, is then impregnated with  $\text{K}_2\text{CO}_3$ . Presumably the potassium promotes the iron and deacidifies the zeolite. The catalyst was formed into extrudate with 15 percent filled binder.

Conversion, product selectivity, isomerization of the pentanes, and percent olefins of the  $\text{C}_4$ 's are plotted as a function of time on stream in Figs. 42-45. Simulated distillations of representative products are shown in Figs. 46-48. Carbon number product distributions of the samples are given in Figs. 49-55. Chromatograms from the simulated distillations of the condensed products are reproduced in Figs. 56-62. Detailed material balances are given in Tables 3A-3C.

The syngas conversion of this catalyst is lower than those of the last two catalysts reported (10011-17 and 10225-3, Fig. 42). Also, its concentration of iron is only 40 percent of theirs. Gram for gram of iron, however, it is more active. Carbon monoxide and hydrogen conversion levels are close, but hydrogen conversion is higher, leading to a hydrogen:carbon monoxide usage ratio greater than 1.0. All the physically mixed catalysts had hydrogen:carbon monoxide usage ratios lower than 1.0, allowing

them to use hydrogen-lean syngas efficiently. The WGS activity of this catalyst is lower, making for higher hydrogen usage. Lower WGS activity was anticipated even though this catalyst has a higher K content, 5 w/w percent compared to 1 w/w percent for catalysts 10011-17 and 10225-3. With much of the potassium going to the zeolite, less of it is available for effectively promoting the iron. Conversion was very steady at 250C and increased with increasing temperature. Higher temperature also increased WGS activity relative to F-T activity. This lowered the hydrogen: carbon monoxide usage ratio even though the F-T product hydrocarbons were more hydrogen-rich.

Hydrogen product selectivity remained constant at 250C, with only a slight increase in the production of "lights" with rising temperature. Methane production was high, 14 percent at 250C. Combined gasoline and diesel yield was lower than with the two previous catalysts, 46 percent at 250C. Most of the drop was due to a change in diesel selectivity: with this catalyst, selectivity to diesel was 3 percent.

Isomerization of pentane decreased rapidly, then increased with rising temperature (Fig. 44). The change in isomerization activity was paralleled by changes in olefin content of the butanes (Fig. 45). With the UCC-109 catalyst (Run 10011-17), this was interpreted as an indication of coke deactivation; in this case, the ethanes and propanes did not follow the trend to be expected if this were coking. The change in selectivity was more likely due to potassium migration into the zeolite, leading to

P

less active isomerization and hydrogen transfer sites. Both LZ-105 and ZSM-5 are known to have strongly acid sites which do not coke rapidly, but are poisoned by alkali.

Products from this catalyst show unusual carbon number distributions. These cannot easily be explained, considering the high activity and the carbon number cut-off capability observed in Task 1 testing. There is generally less of the C<sub>10</sub>-C<sub>20</sub> product and more of the C<sub>20</sub>-C<sub>30</sub>. Perhaps the C<sub>10</sub><sup>+</sup> product dimerizes (possibly on the surface of the zeolite crystal) into the C<sub>20</sub><sup>+</sup> range. This effect has been found before with some medium-pore materials, but never fully explained.

The quality of the gasoline produced should be quite high, as can be seen from Figs. 56-62. The condensed liquid products of this catalyst are all highly isomerized, even though the pentane was not. The UCC-104 catalyst was superior to this one, however, since it produced a better yield of gasoline and diesel oil.

RUN 10225-01

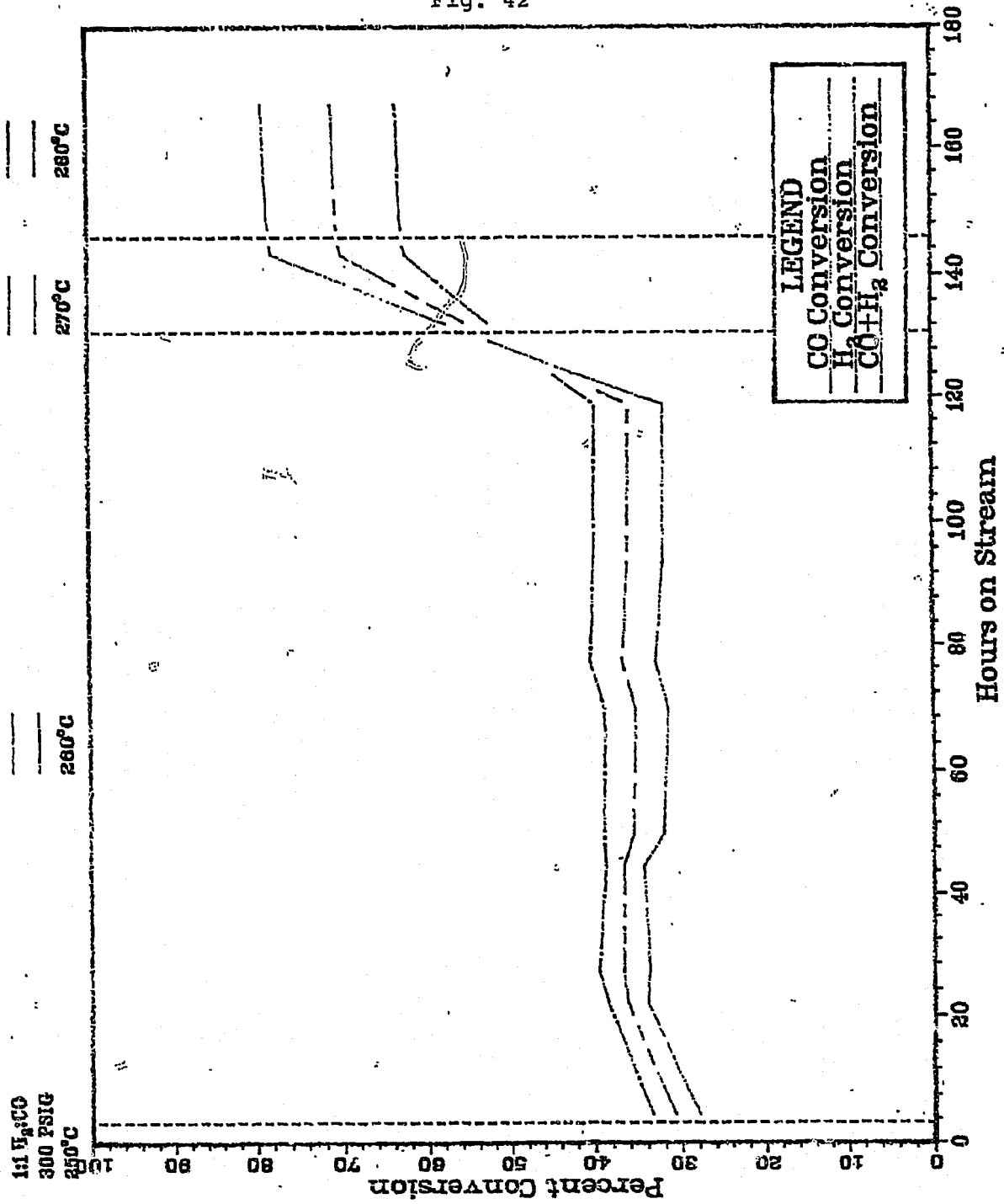
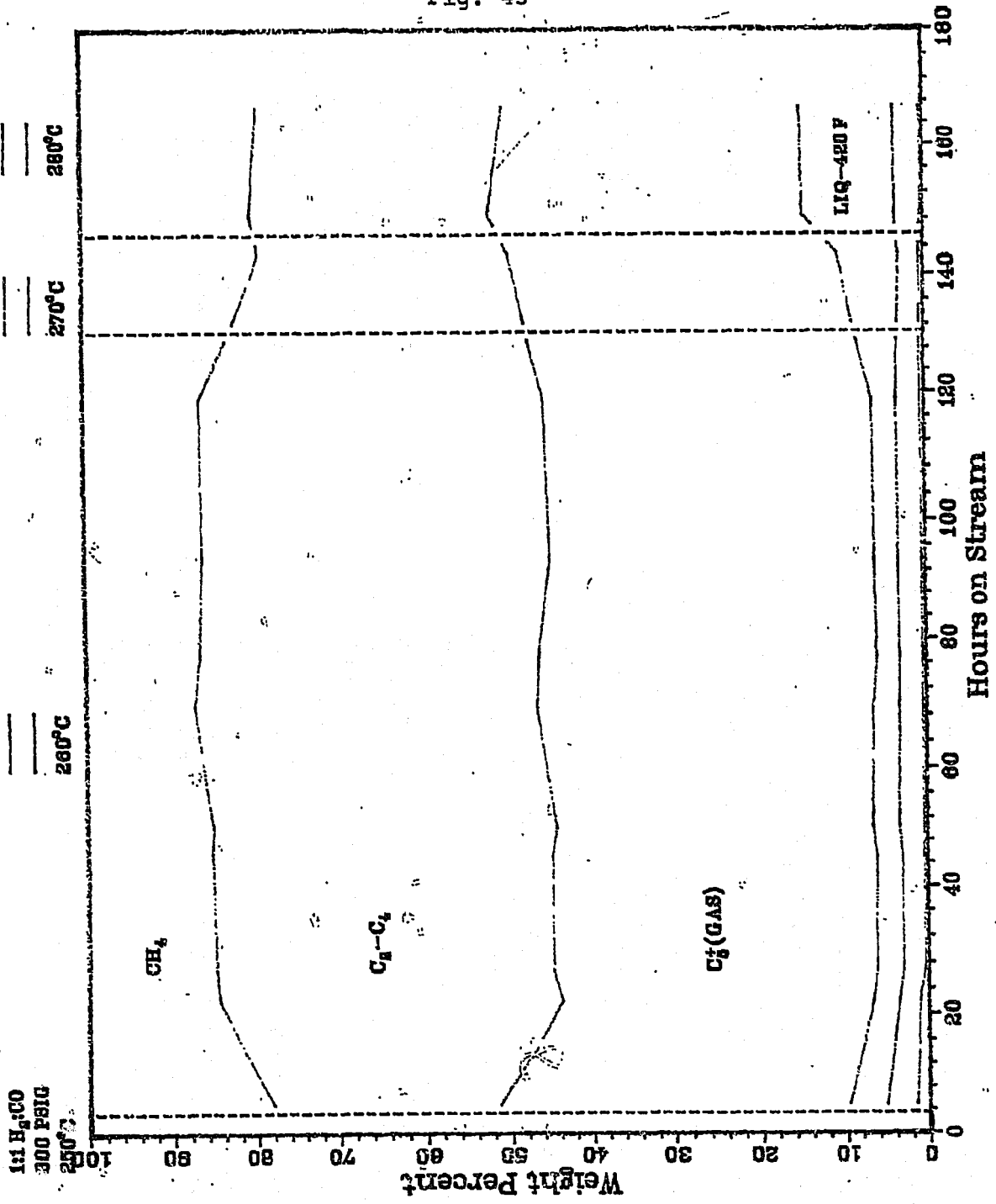


Fig. 42

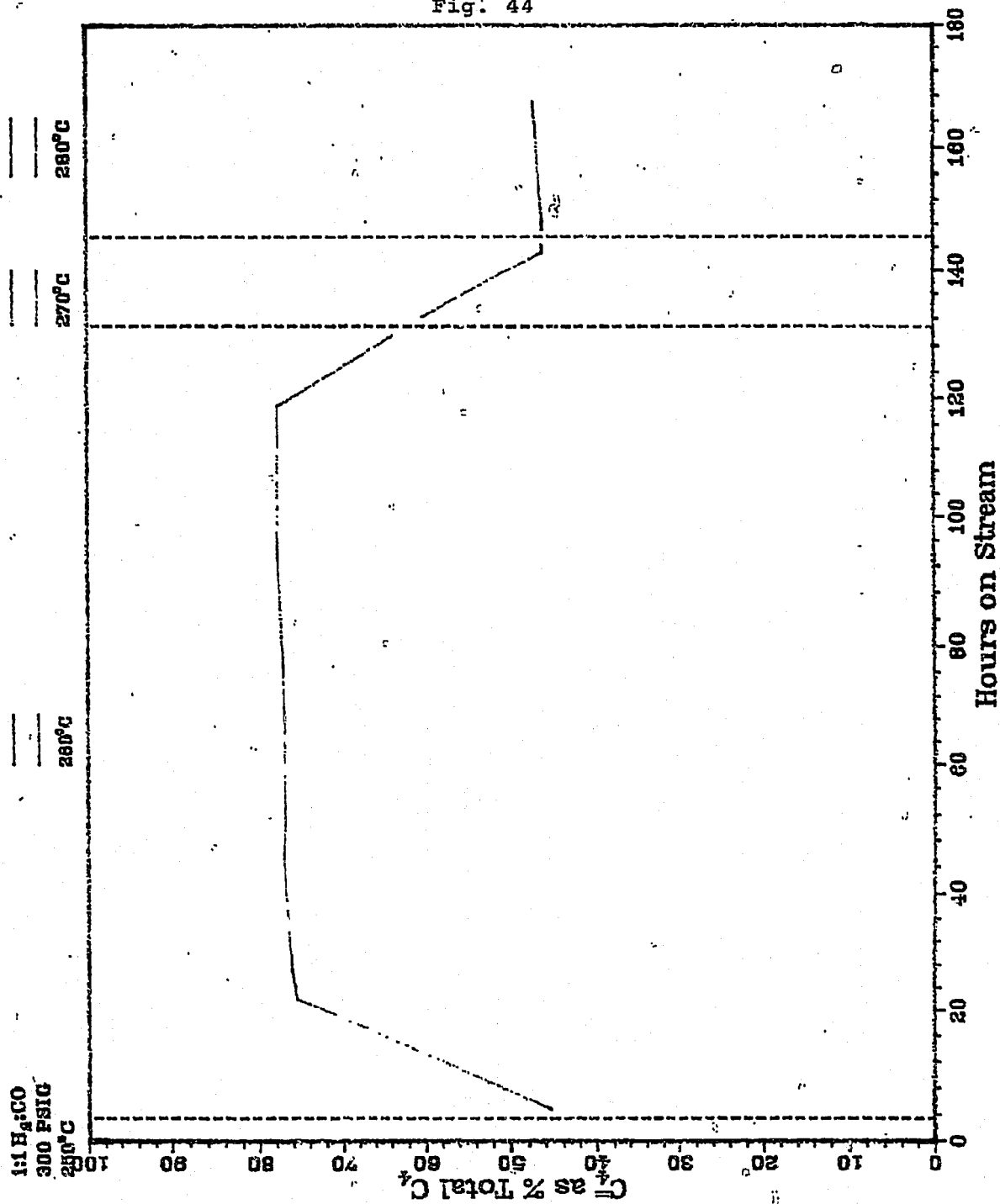
RUN 10225-01

Fig. 43



RUN 10225-01

Fig. 44



RUN 10225-01

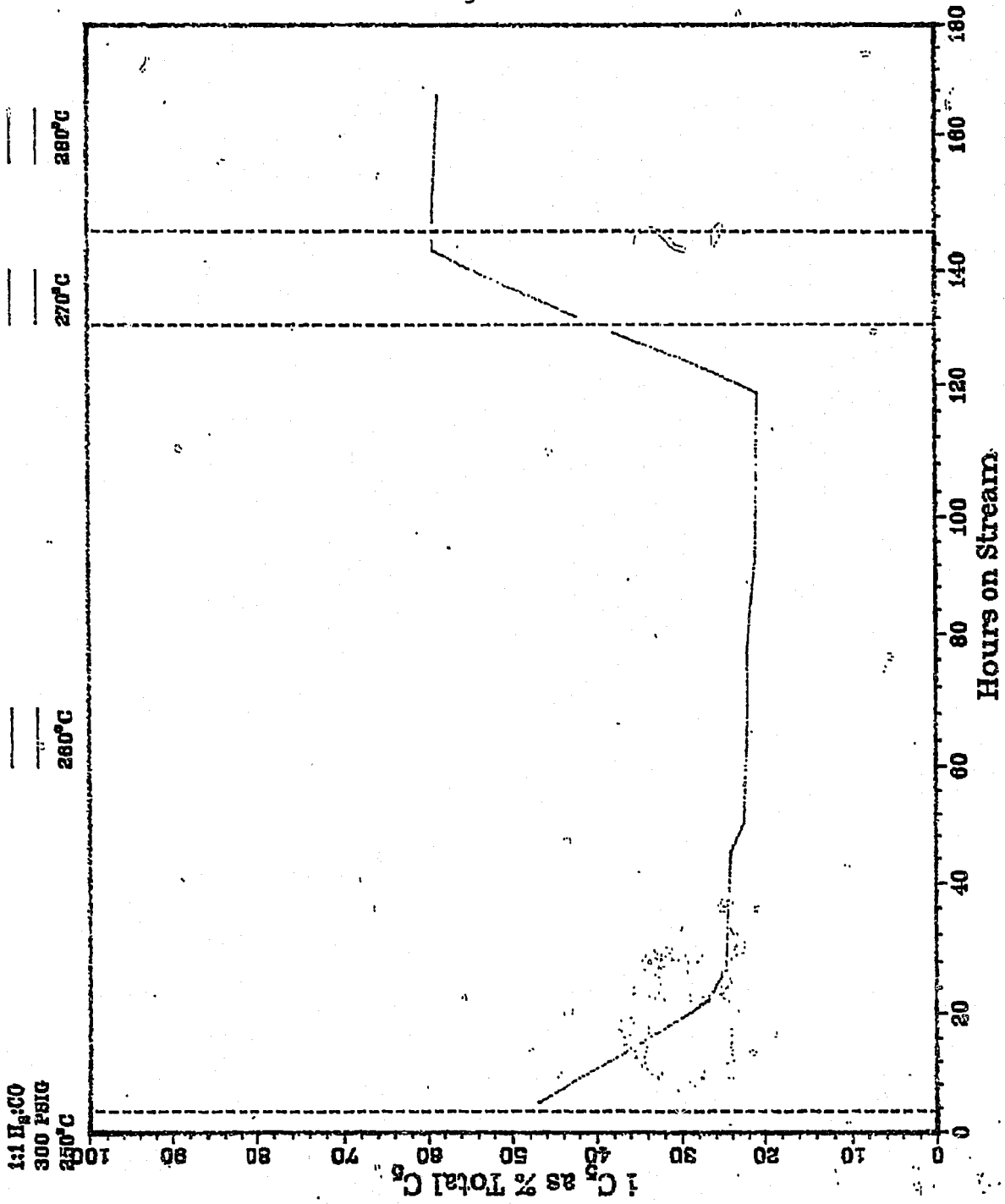


Fig. 45



Fig. 46

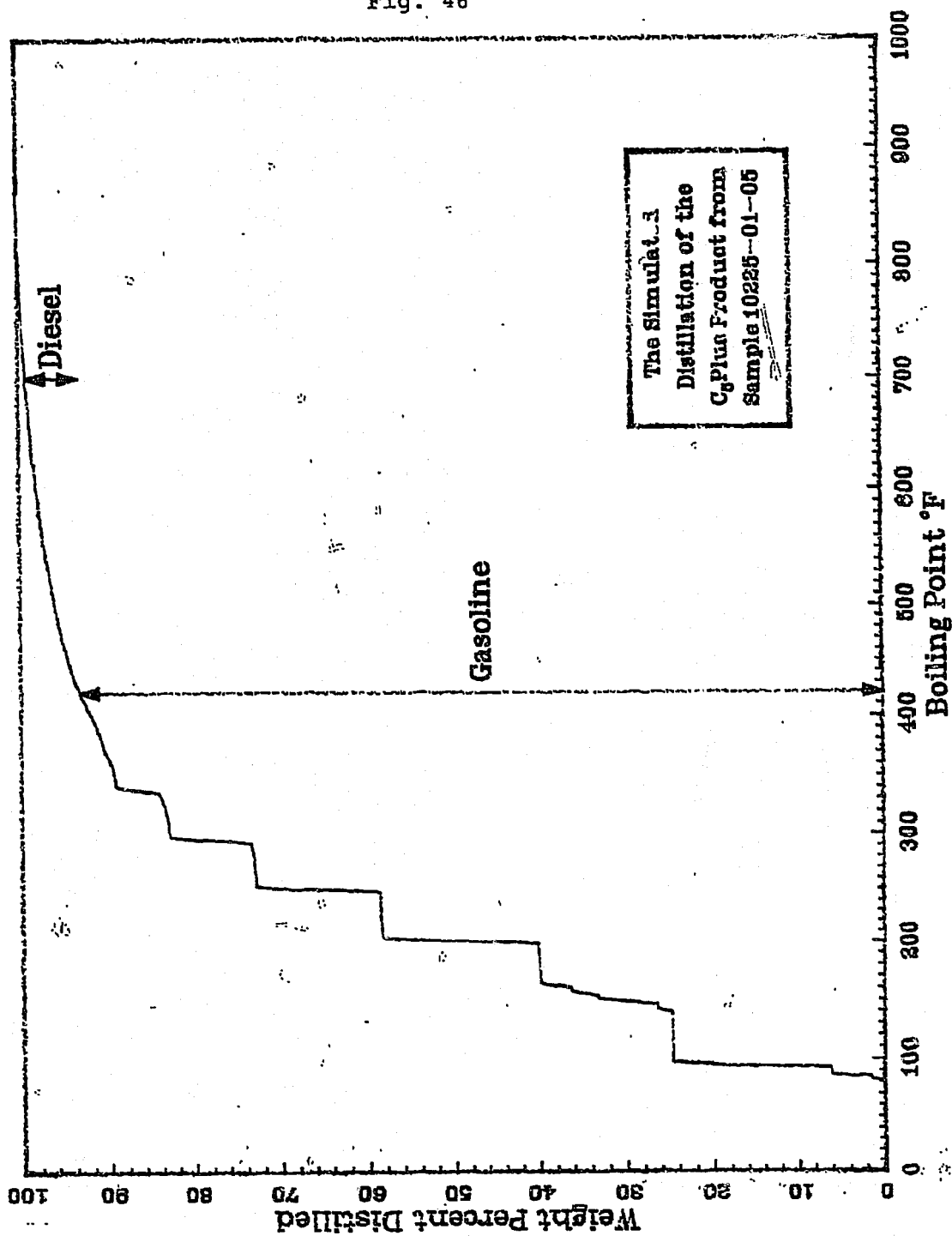


Fig. 47

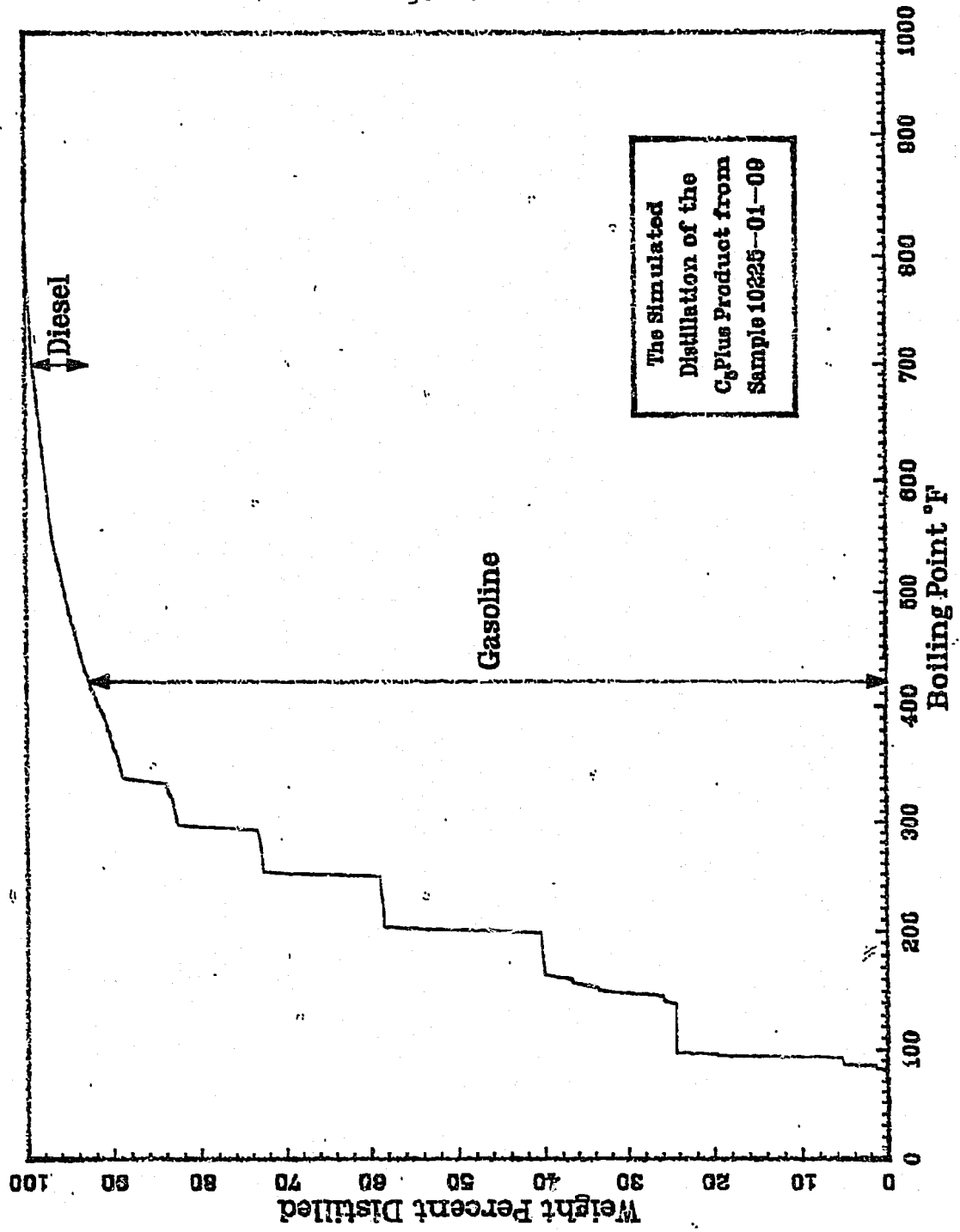
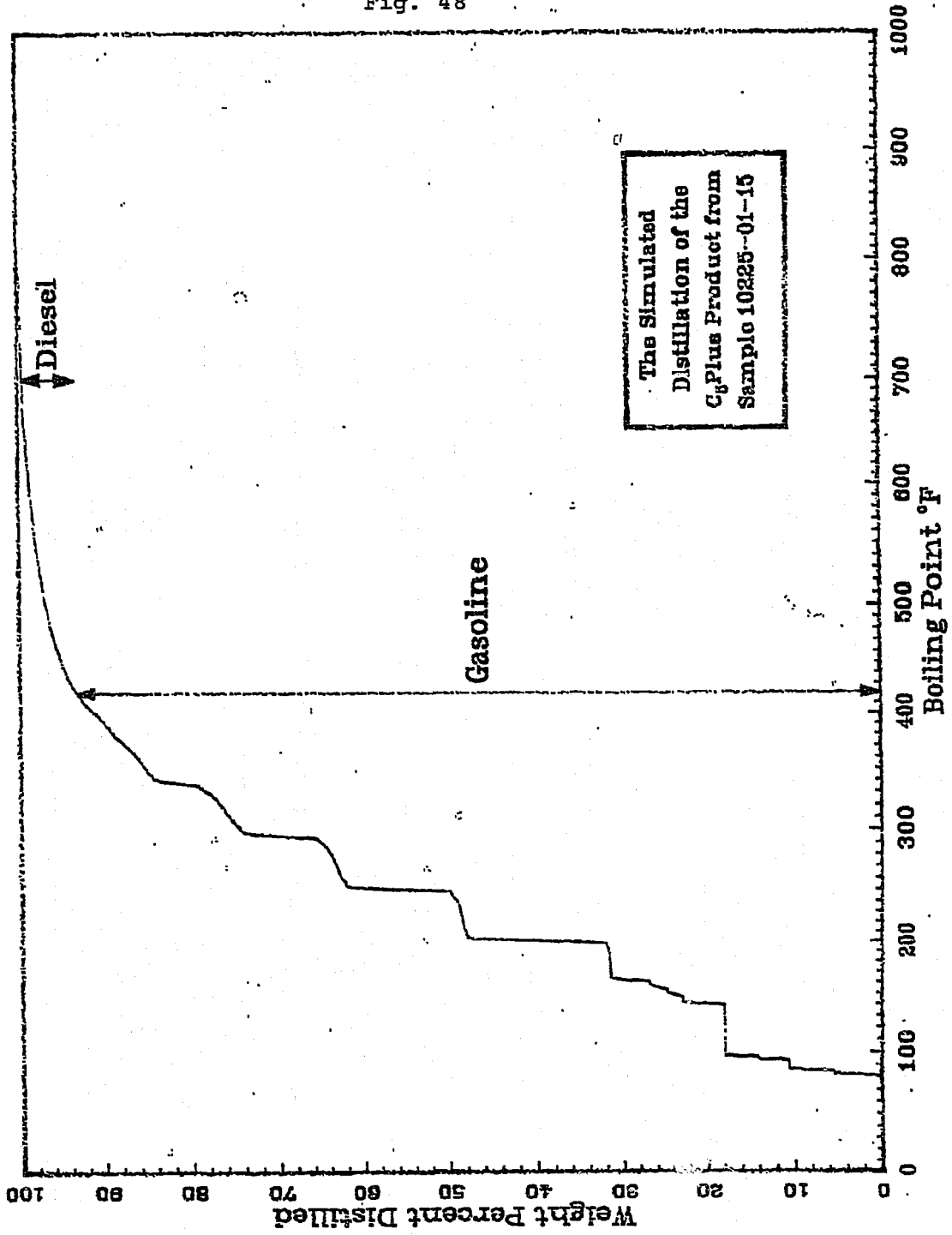


Fig. 48



The Simulated  
Distillation of the  
C<sub>6</sub> Plus Product from  
Sample 10225-01-15

Gasoline

Diesel

Fig. 49 .

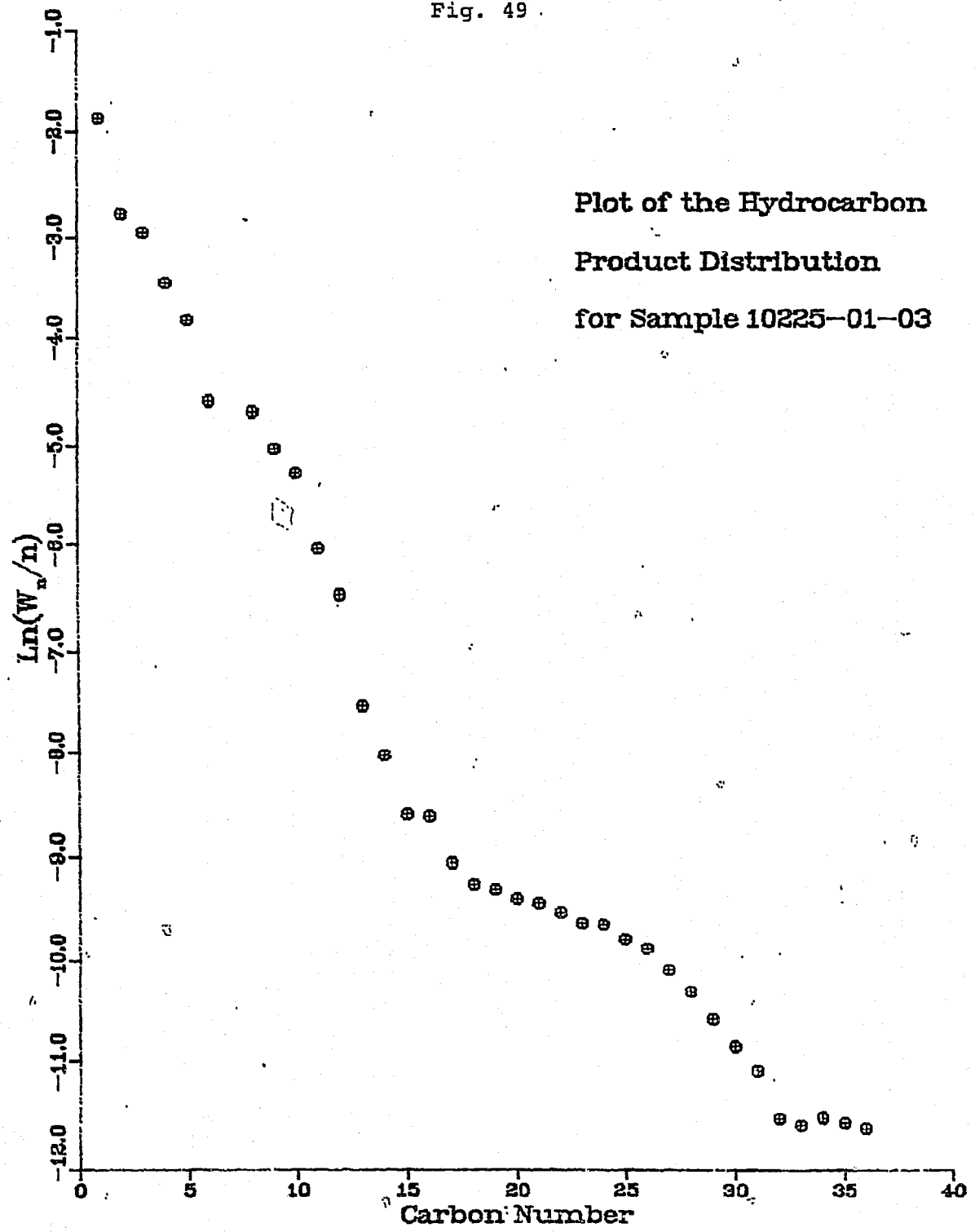


Fig. 50

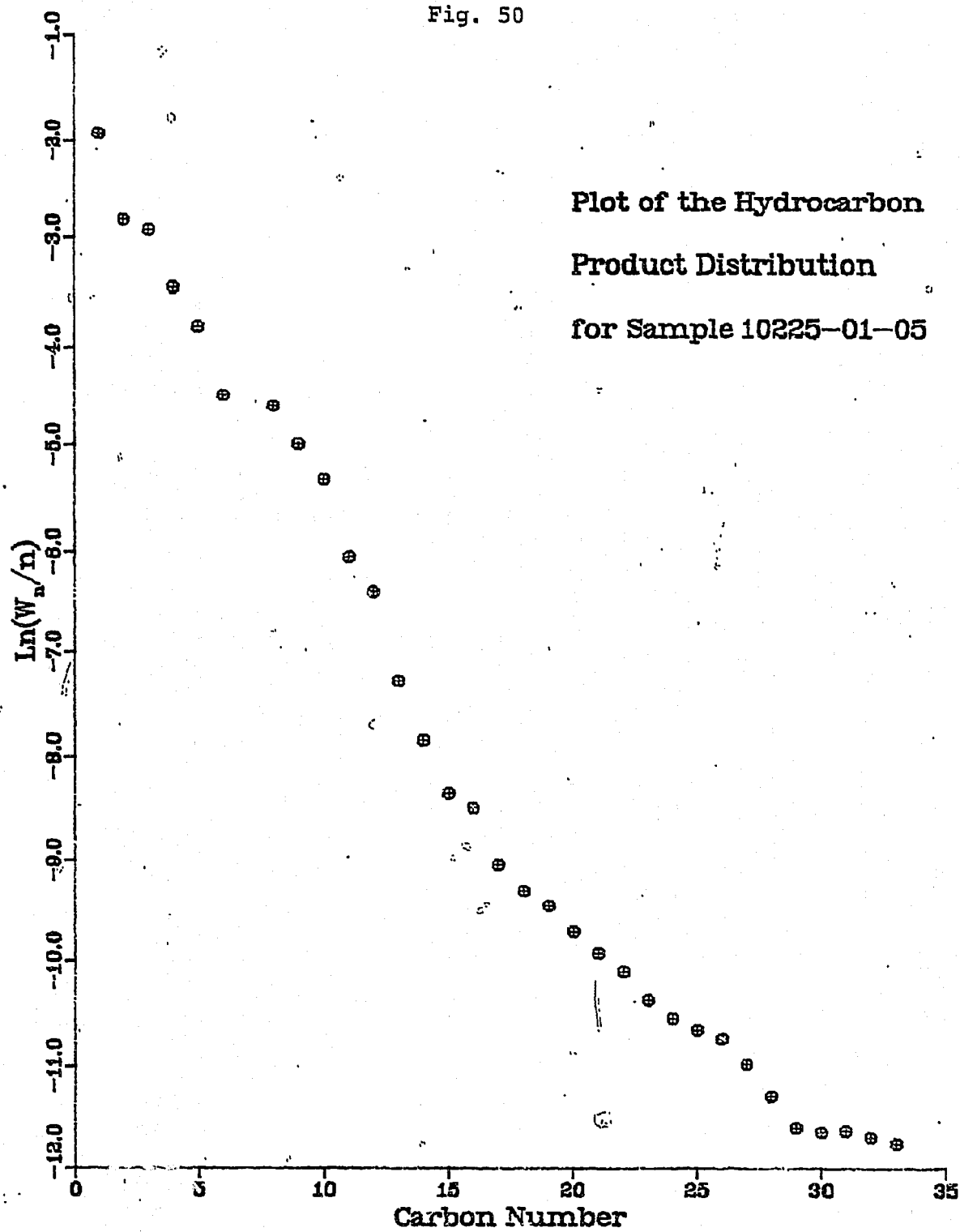


Fig. 51

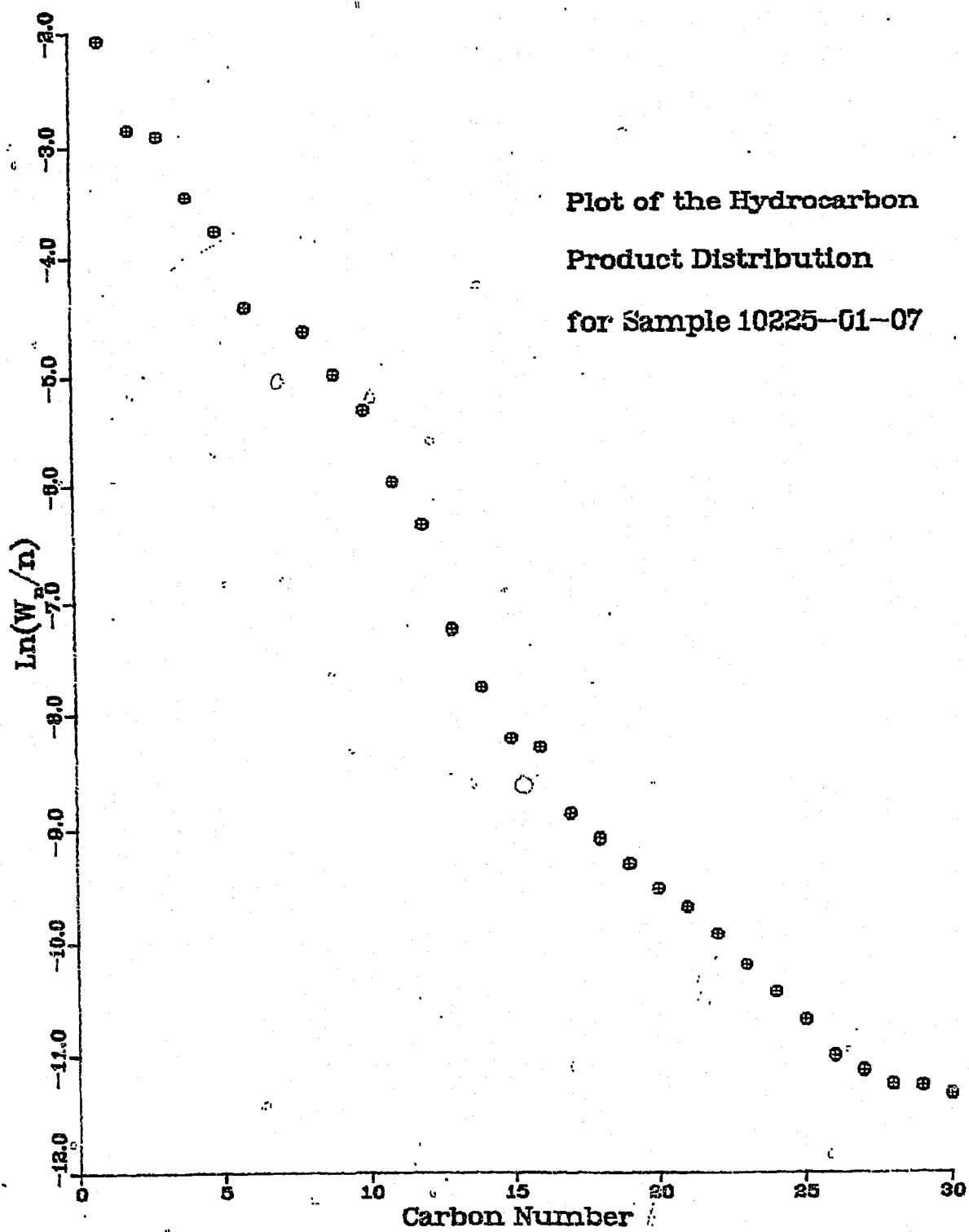


Fig. 52

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-01-09

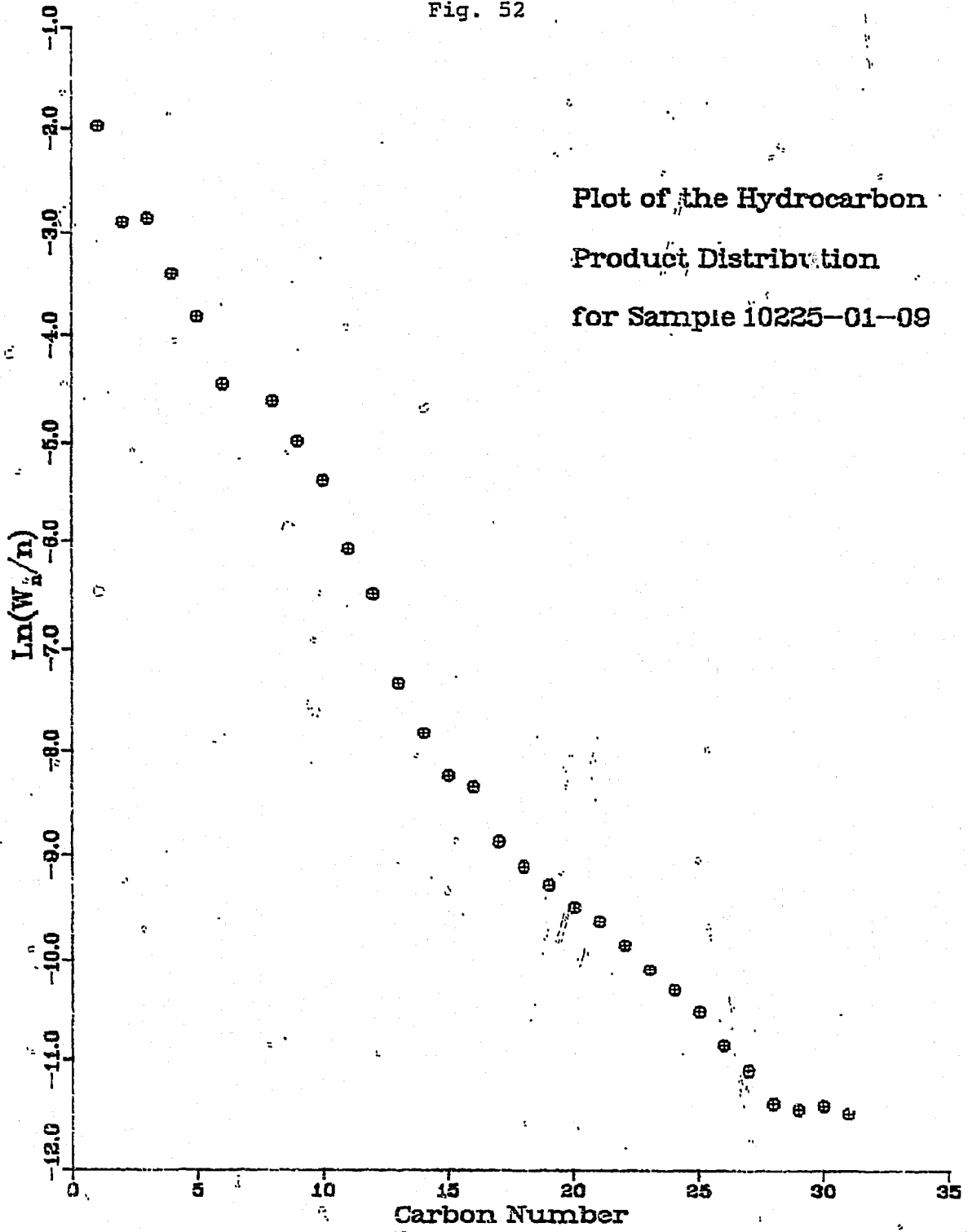


Fig. 53

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-01-11

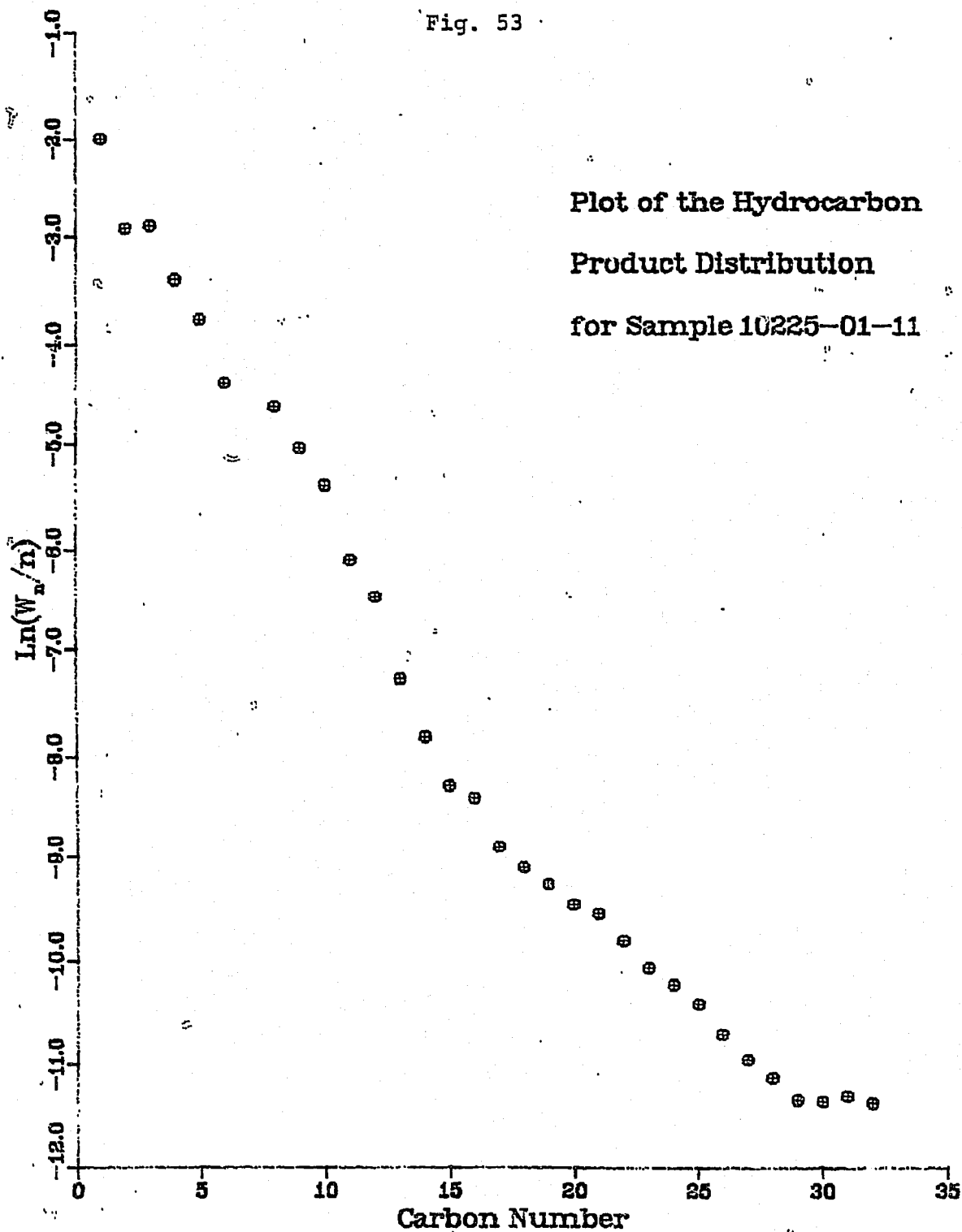




Fig. 54

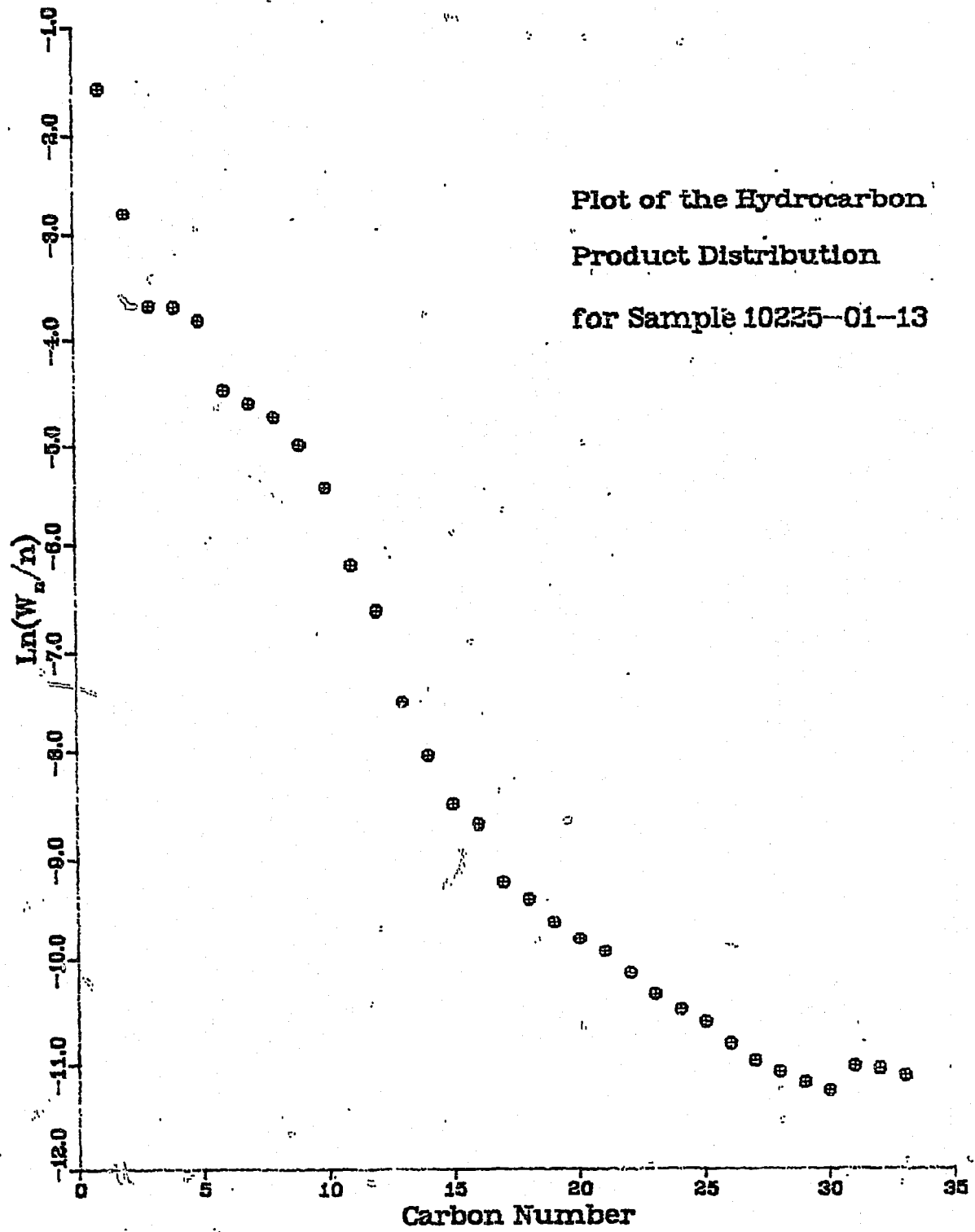


Fig. 55

Plot of the Hydrocarbon  
Product Distribution  
for Sample 10225-01-15

