

Appendix A. CATALYST TESTING

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I. INTRODUCTION

This report presents the results of eight catalyst tests conducted from May through July, 1984, the Fourteenth Quarter of this contract.

All the catalysts tested contained cobalt intimately mixed with the shape-selective component UCC-103. All but one (Catalyst 1) also contained physically mixed shape-selective component UCC-101, which has been found to have so little effect in this form as to be almost inert.

In addition, Catalyst 1 contained the additive X₄; Catalysts 2 and 3 contained X₈; Catalysts 4, 5, 7 and 8 contained both X₄ and X₈; and Catalyst 6 contained X₄ and potassium.

X₈ is a new additive which is chemically similar to X₆, one of the components of Eleventh Quarterly Report Catalyst 4 (Run 11677-3). X₆ was not effective when first tested in an intimately mixed catalyst (Third Annual Report Catalyst 5, Run 11723-4), and X₈ was developed for greater compatibility with the intimately mixed formulation.

The X₄ in two catalysts (1 and 5) was obtained from the same source as that successfully used in the exceptionally stable Third Annual Report Catalyst 6 (Run 11677-11). In the four other catalysts which contained it (4, 6 through 8), the X₄ was obtained from the same source as that used in Thirteenth Quarterly Re-

port Catalyst 4 (Run 11688-17), which was unsuccessful.

Catalyst 1 (Run 11723-17) was subjected to varied process conditions following the initial portion of the run, to test the effect of pressure and temperature changes on conversion, selectivity and stability.

Catalyst 7 (Run 11885-02), which contained cobalt, thorium, UCC-103, UCC-101, X₄ and X₈, was tested continuously for one month on stream to obtain additional deactivation data.

Two data items have been added to the tables in this report. One is the Schulz-Flory alpha, as calculated from the model. The other is the weight percent of methane which, according to the model, the catalyst should be producing. Both are compared with the experimental values. The second comparison is useful in explaining the selectivity changes which accompany deactivation, and especially in comparing two catalysts with different usage ratios or activity levels.

2. Run 1 (11723-17) with Catalyst 1 (Co/Th/X₄/UCC-103)

This catalyst is similar to the highly stable Third Annual Report Catalyst 6 (Run 11677-11), with approximately the same levels of cobalt (about 4 percent), thorium and X₄, but with two principal differences.

First, it omits the second molecular sieve UCC-101. In the last quarter it was shown that a second molecular sieve has little if any influence on either the selectivity or the stability of the cobalt/thorium/X₄+UCC-103 catalyst.

Second, the thorium and X₄ were intimately mixed with more UCC-103 than in Third Annual Report Catalyst 6, but with a cobalt/thorium catalyst this does not seem to present a problem. The X₄ was added to the catalyst after the cobalt and thorium. However, the proportion of cobalt to X₄, or of UCC-103 to X₄, may significantly affect the catalyst's stability. In this catalyst the ratio of cobalt to X₄ was similar to that in Third Annual Report Catalyst 6, but the ratio of UCC-103 to X₄ was considerably different.

The X₄ used in this catalyst was obtained from the same source as that used in Third Annual Report Catalyst 6, not from the source used for Thirteenth Quarterly Report Run 11677-17 and four other runs in this quarter.

The intimately mixed cobalt/thorium/X₄+UCC-103 was bonded

with 15 weight percent SiO₂, then formed as 1/8-inch extrudate.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. A1-4. Simulated distillations of the C₅⁺ product are plotted in Figs. A5-10. Carbon number product distributions are plotted in Figs. A11-34. Chromatograms from simulated distillations are reproduced in Figs. A35-40. Detailed material balances appear in Tables A1-5.

The syngas conversion activity was fairly constant, deactivating slowly. If Sample 5, taken when the temperature was anomalously high, is disregarded, the H₂ conversion decreased by one percentage point every 87 hours. The CO conversion is calculated to increase one percentage point every 185 hours, but the linear regression yields a very low correlation coefficient, indicating that this trend may not be real. Taking only the data following Sample 5, the H₂ conversion decreased one percentage point every 64 hours, the CO conversion decreased one percentage point every 275 hours, and the total CO+H₂ conversion decreased one percentage point every 104 hours.

The specific activity was 0.7, substantially lower than the 0.9 of Run 11677-11; since the two cobalt levels were approximately the same, this catalyst uses the cobalt less efficiently. The water gas shift activity was also low, with a H₂:CO usage ratio of more than 2.1:1. The catalyst of Run 11677-11 was not much better in this respect, with a ratio of 2.0:1, but it was more stable. In this catalyst the X₄ seems to have been sub-

stantially less effective at stabilizing the cobalt than it was in Run 11677-11. Both the X₄ and the cobalt are interacting with more UCC-103, but the X₄ seems to be interacting more with the JCC-103 and less with the cobalt. This suggests the possibility that an effective catalyst requires a constant ratio of X₄ to UCC-103 but not of X₄ to cobalt.

The first part of the run, of approximately 295 hours duration, was conducted at 300 psig and 260C. To test the effects of changes in pressure and temperature on conversion, selectivity and stability, the run was then continued approximately 305 hours longer, in five additional stages:

Stage 2 (app. 50 hrs):	500 psig	260C
Stage 3 (app. 70 hrs):	300 psig	260C
Stage 4 (app. 75 hrs):	500 psig	270C
Stage 5 (app. 50 hrs):	290 psig	270C
Stage 6 (app. 60 hrs):	500 psig	280C

In Stage 2 the reactor pressure was raised to 500 psig in an attempt to increase the conversion rate. The conversion did increase slightly at first, but not as much as the mathematical model predicts it should, so that the specific activity decreased. (This seems to be generally true of this model: it remains valid as long as the pressure is held constant, and fails when the pressure is changed.) At 500 psig, the deactivation rate was significantly higher than at 300 psig.

In Stage 3, with the pressure restored to 300 psig, the deactivation rate was again very low. The conversion, however, was substantially lower following the deactivation in Stage 2.

In Stage 4, when the pressure was again raised to 500 psig

and the temperature raised to 270C as well, the catalyst again deactivated rapidly, although not as rapidly as in Stage 2. In Stage 5 the pressure was reduced to 300 psig with the temperature maintained at 270C. During the approximately two days under these conditions the conversion increased significantly. The specific activity of 0.48 at 525 hours on stream, in the latter half of Stage 5, did not quite equal the level of 0.53 it had reached at 404 hours on stream near the end of Stage 3, shortly before pressure and temperature were raised to 500 psig, 270C. At higher temperature, apparently, the deactivation due to higher pressure may be reversible.

In Stage 6, at 500 psig and 280C, the catalyst again deactivated, at a rate close to that in Stage 4 (500 psig, 270C).

It is generally accepted that Fischer-Tropsch catalysts, notably those with iron which have been especially well studied, undergo irreversible changes with increased reaction temperature. It would not therefore be unreasonable to suppose that increased pressure could alter the catalyst as well. It is true that the iron-containing catalyst contains a complex mixture of metal, oxide and carbide phases, whereas cobalt seems generally to be in the metallic state. The cobalt is associated with surface carbon which may be affected by pressure.

Methane production was fairly high at about 16 percent. But since the H₂:CO ratio inside the reactor was also high--about 0.6:1, for which the mathematical model predicts about 20 percent methane--the actual output was only 80 percent of what the model

predicts. The catalyst of Run 11677-11 produced only 13 percent methane, but this was 90 percent of what the model predicts since higher conversion resulted in a lower H₂:CO ratio in the reactor. The methane production of the present catalyst was fairly stable, increasing by one percentage point every 147 hours on stream, but not quite as stable as in Run 11677-11. It is hard to say which of the two catalysts would produce less methane at equal H₂:CO ratios; judging from the model alone it should be this one.

The production of C₂-C₄ was fairly low, and lower than in Run 11677-11. As a result, and although its methane production was three percentage points higher, this catalyst produced about 70 percent C₅⁺ as against 69 percent for the catalyst of Run 11677-11. Co/Th/X₄ catalysts generally produce more C₂-C₄'s than do Co/Th catalysts. In this case, however, the X₄ seems to have had less of this effect, possibly because it was interacting with more UCC-103, and the resulting selectivity more nearly resembles that of a Co/Th catalyst. As with the conversion and the methane production, the production of C₅⁺ was not as stable as in Run 11677-11. Production of C₅⁺ decreased by one percentage point every 51 hours, mostly due to a decrease in diesel production of one percentage point every 46 hours. Production of gasoline actually increased by one percentage point every 80 hours, offset by a one percentage point loss of heavies every 96 hours. The result was a more stable production of motor fuels, with a loss of one percentage point every 108 hours. In addition, the motor fuels grew richer in gasoline with time on stream. Taking a cut

point of 420F between gasoline and diesel, twice as much gasoline as diesel was produced; at a cut point of 350F the two were equal in quantity, at least early in the run.

The five changes in process conditions appear to demonstrate that raising the pressure accelerates the deactivation rate, and that raising the temperature, as expected, impairs the C₅⁺ production.

As in previous tests, UCC-103 was almost devoid of isomerization activity; see, for example, Fig. A3 and the chromatograms of the simulated distillations (Figs. A35-40). The olefin content was low and decreased with time on stream, which is not characteristic of Co/Th/X₄ catalysts. The hydrocarbon product distribution, except for the excess methane, follows a Schulz-Flory pattern.

This catalyst is not as stable as some of the X₄ catalysts previously tested, but it is superior to many of those without X₄. It seems likely that the proportion of X₄ to UCC-103 is more important in this formulation than the proportion of X₄ to cobalt.

RUN 11723-17

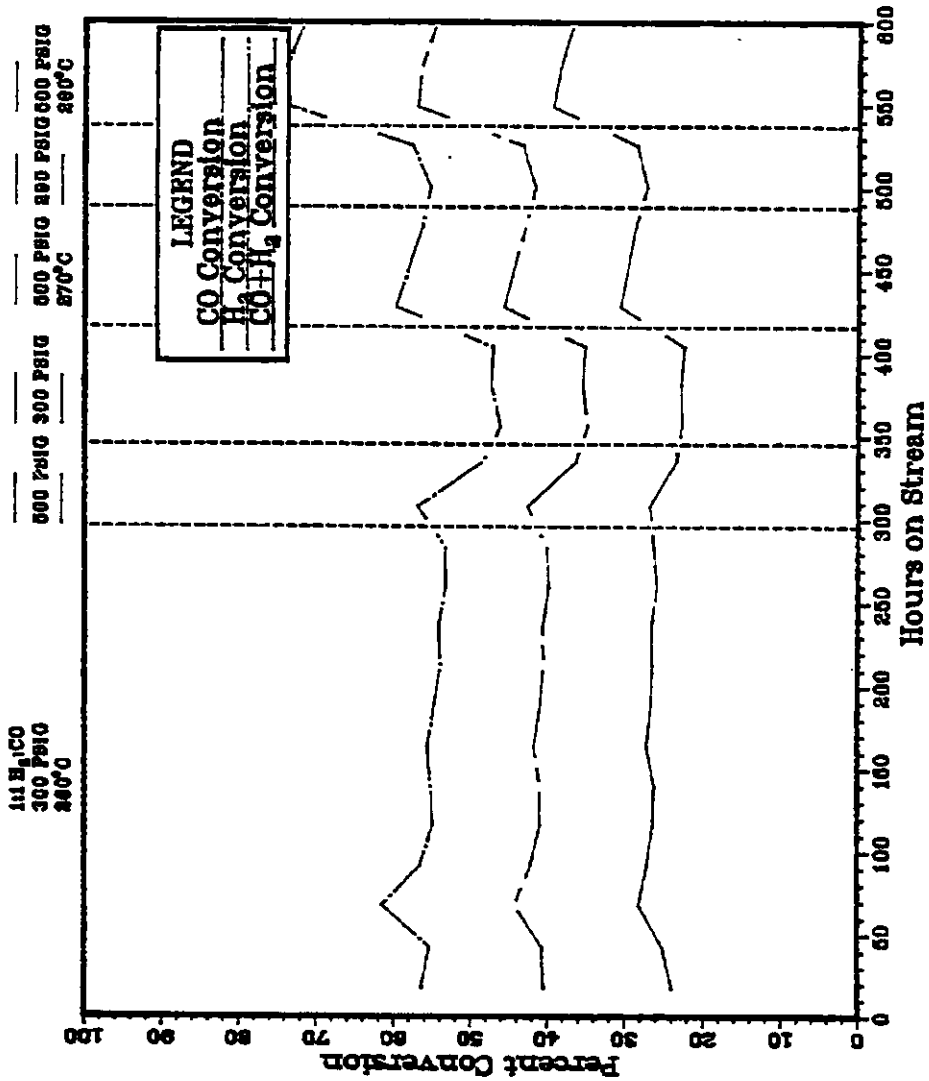


Fig. A1

RUN 11723-17

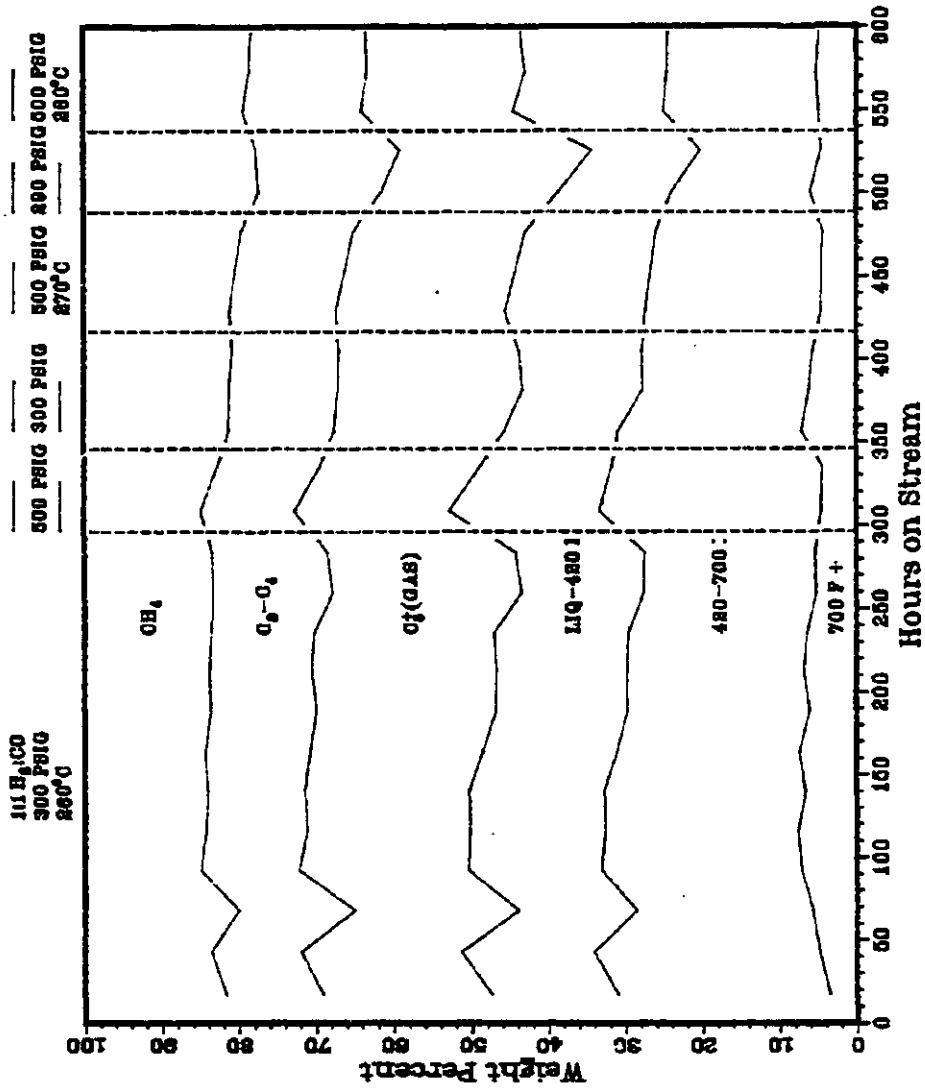


Fig. A2

RUN 11723-17

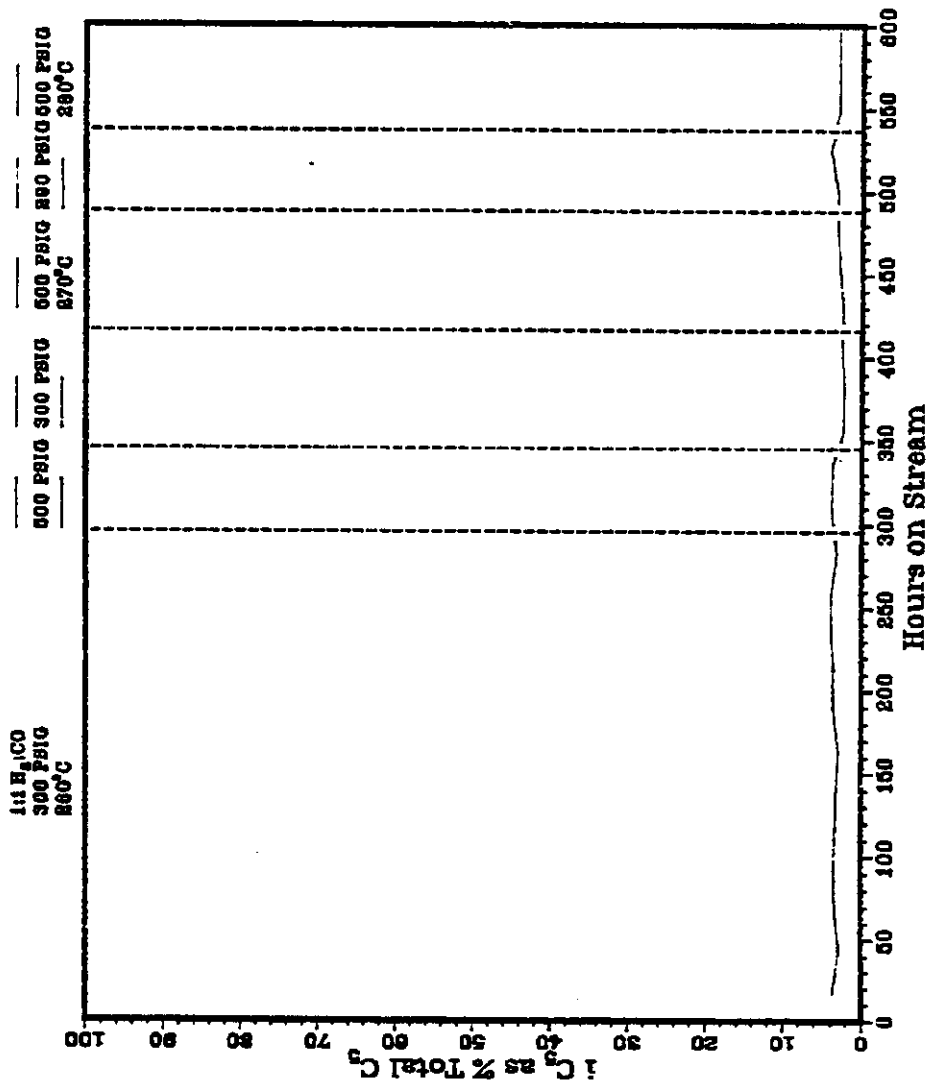


Fig. A3

RUN 11723-17

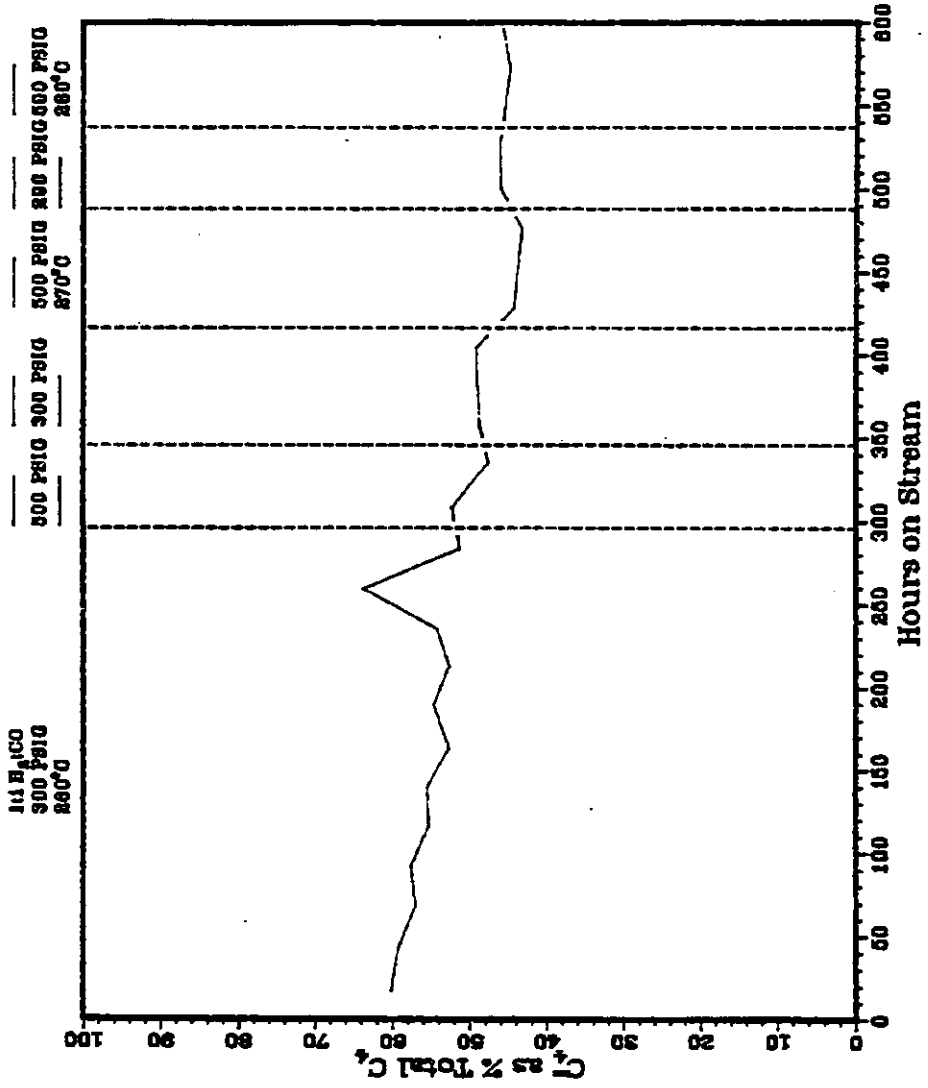
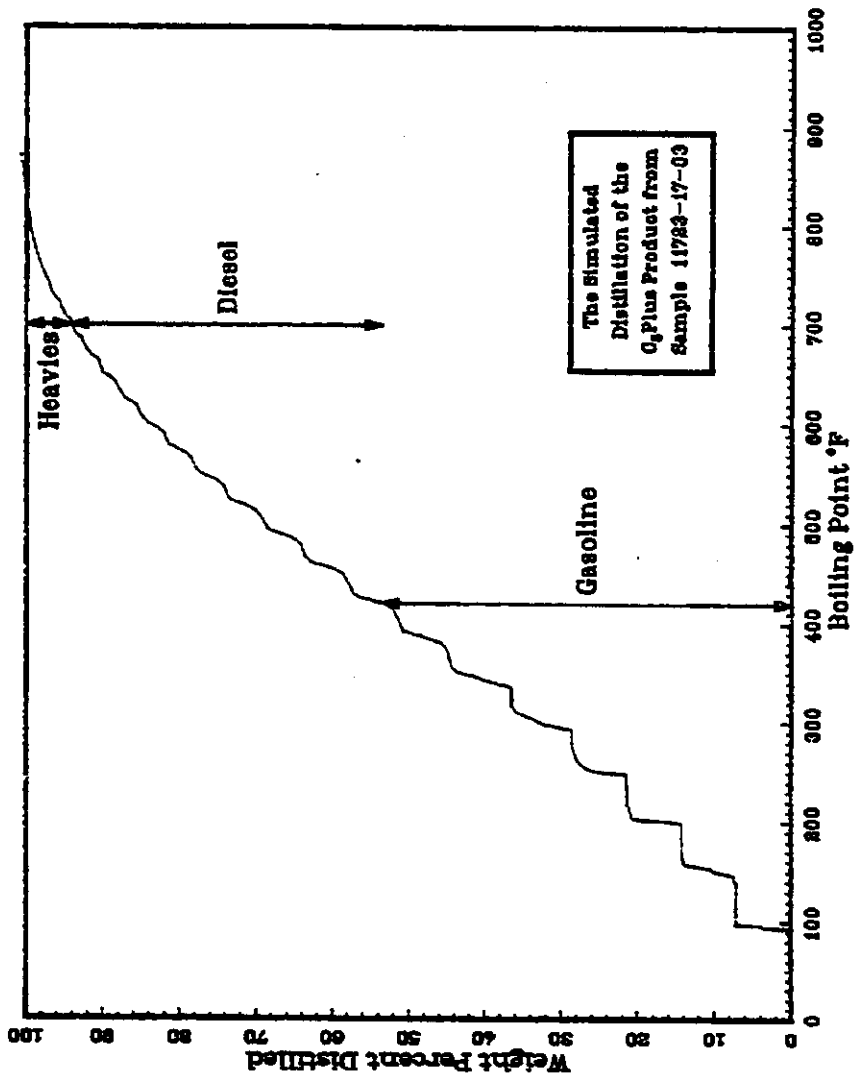
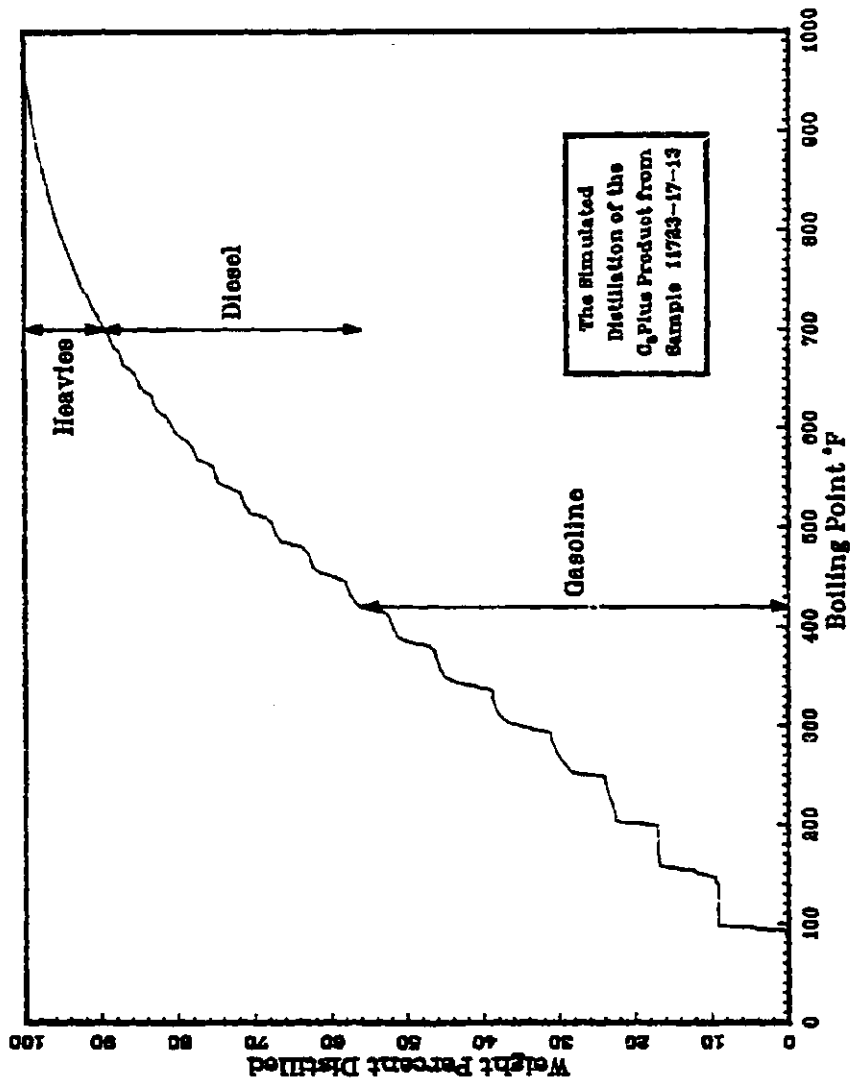


Fig. A4



The Simulated
Distillation of the
O₂ Plus Product from
Sample 11783-17-03

Fig. A5



The Simulated
Distillation of the
C₁₂+ Product from
Sample 11723-17-13

Fig. A6

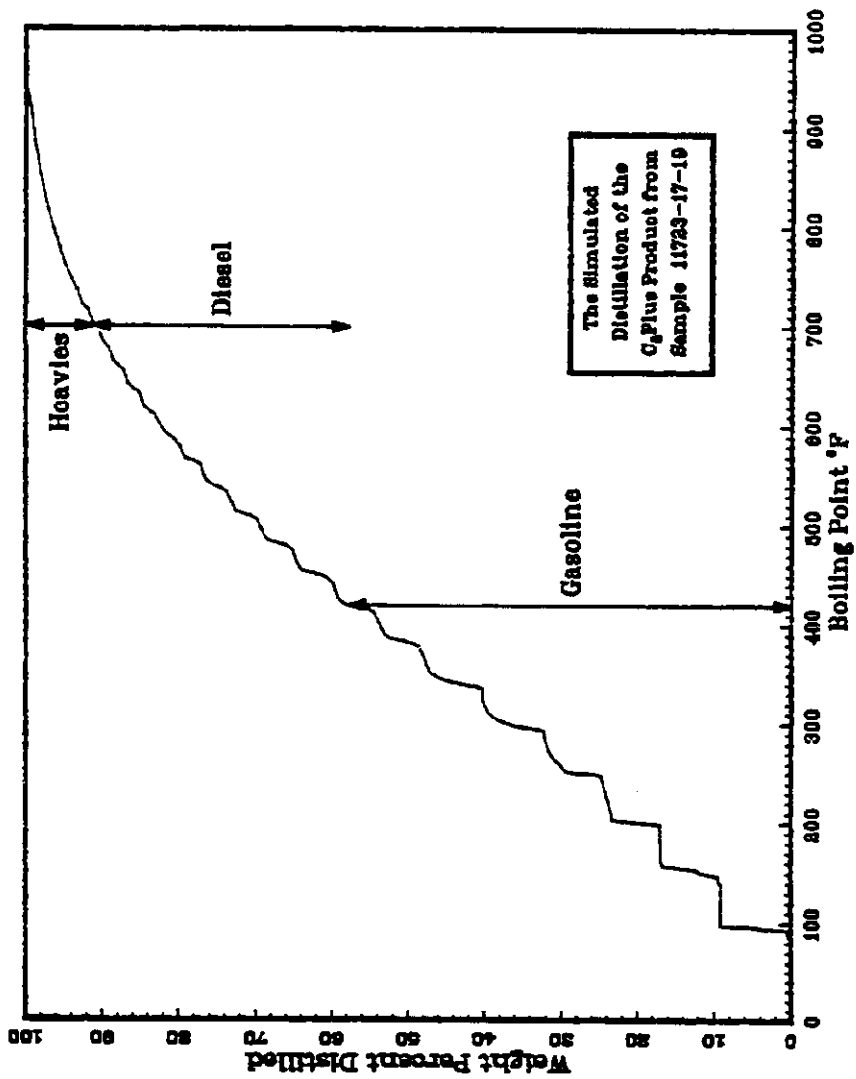


Fig. A7

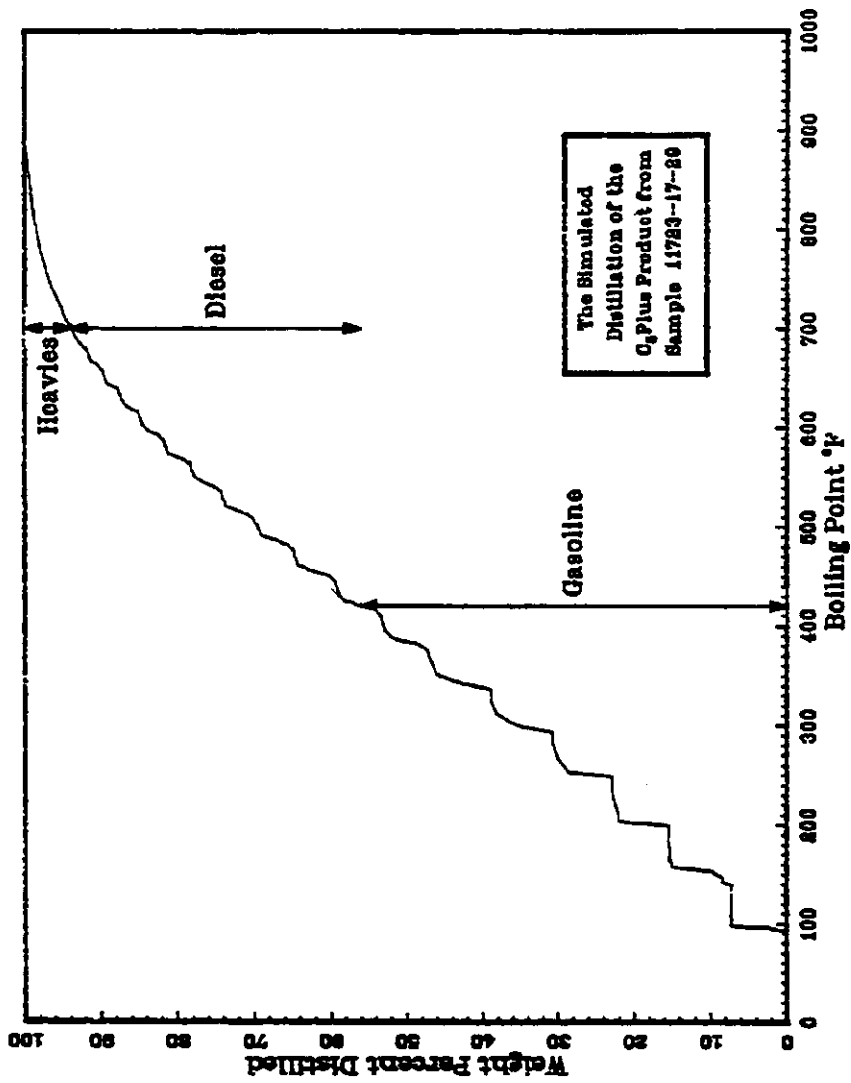


Fig. A8

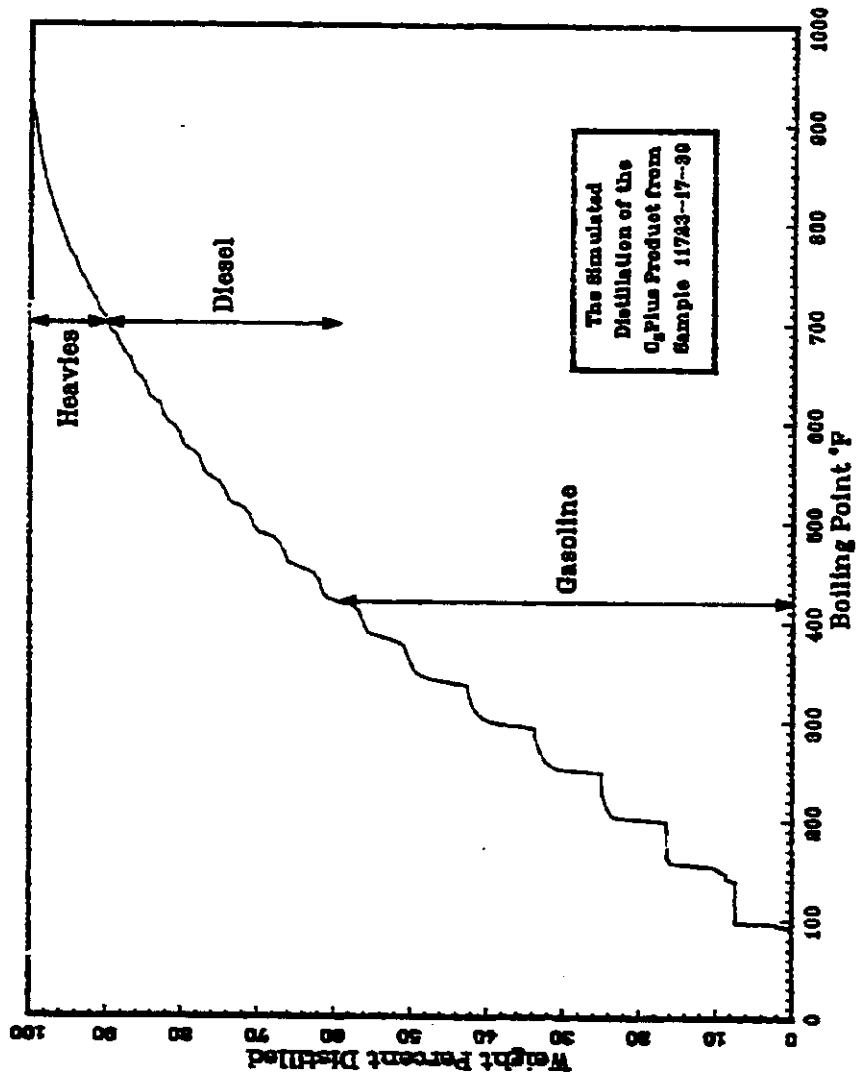


Fig. A9

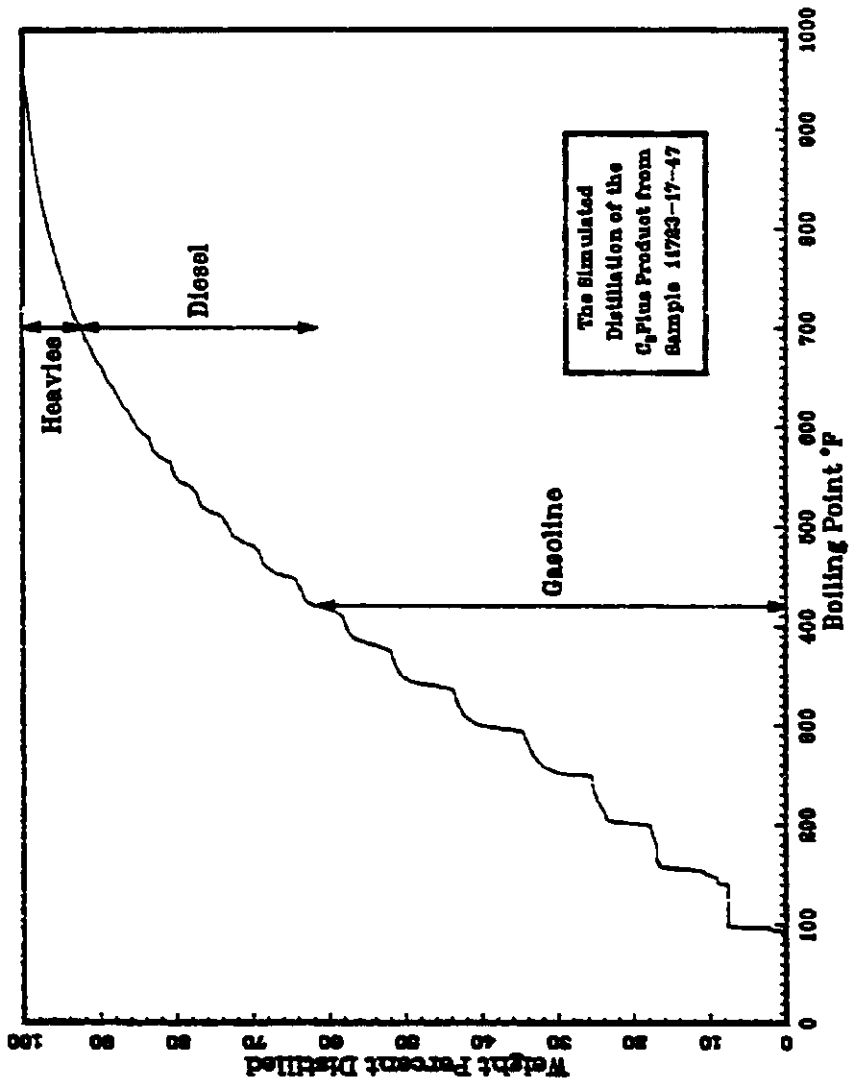


Fig. A10

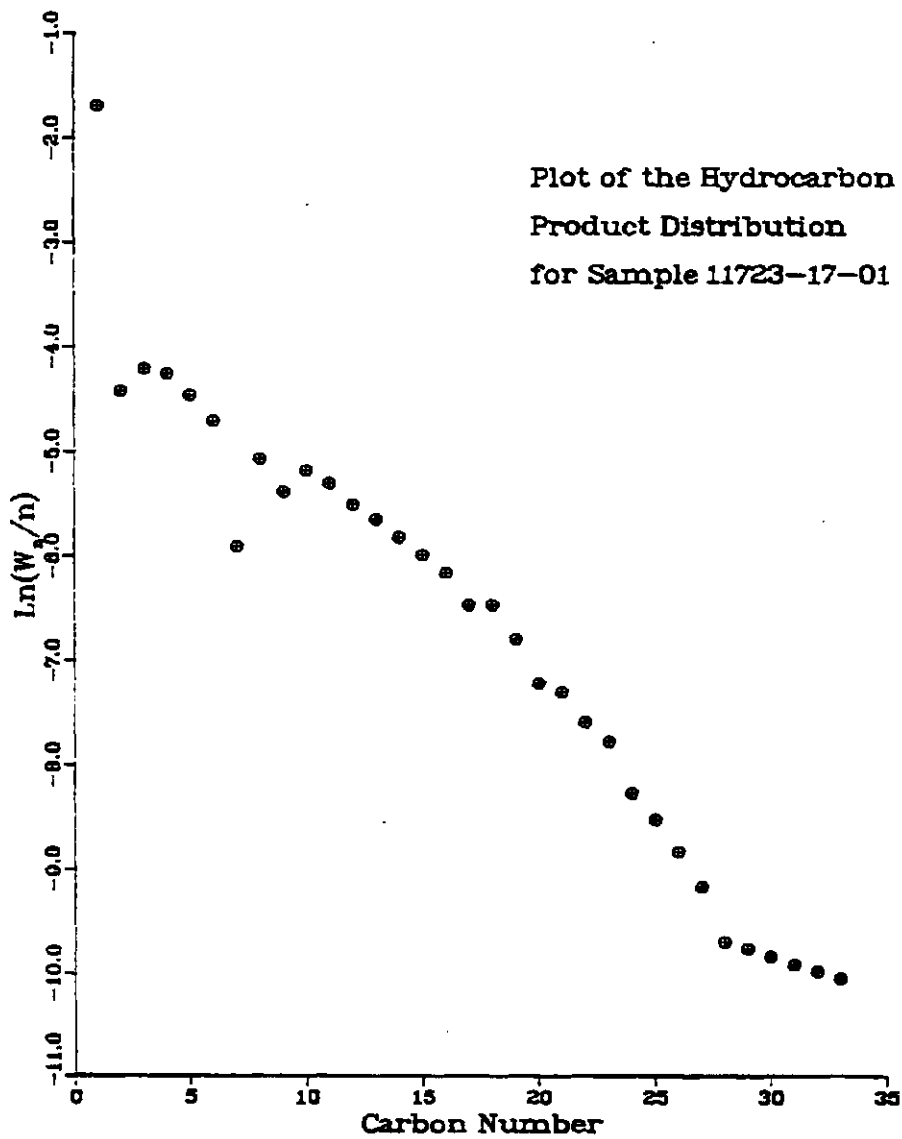


Fig. A11

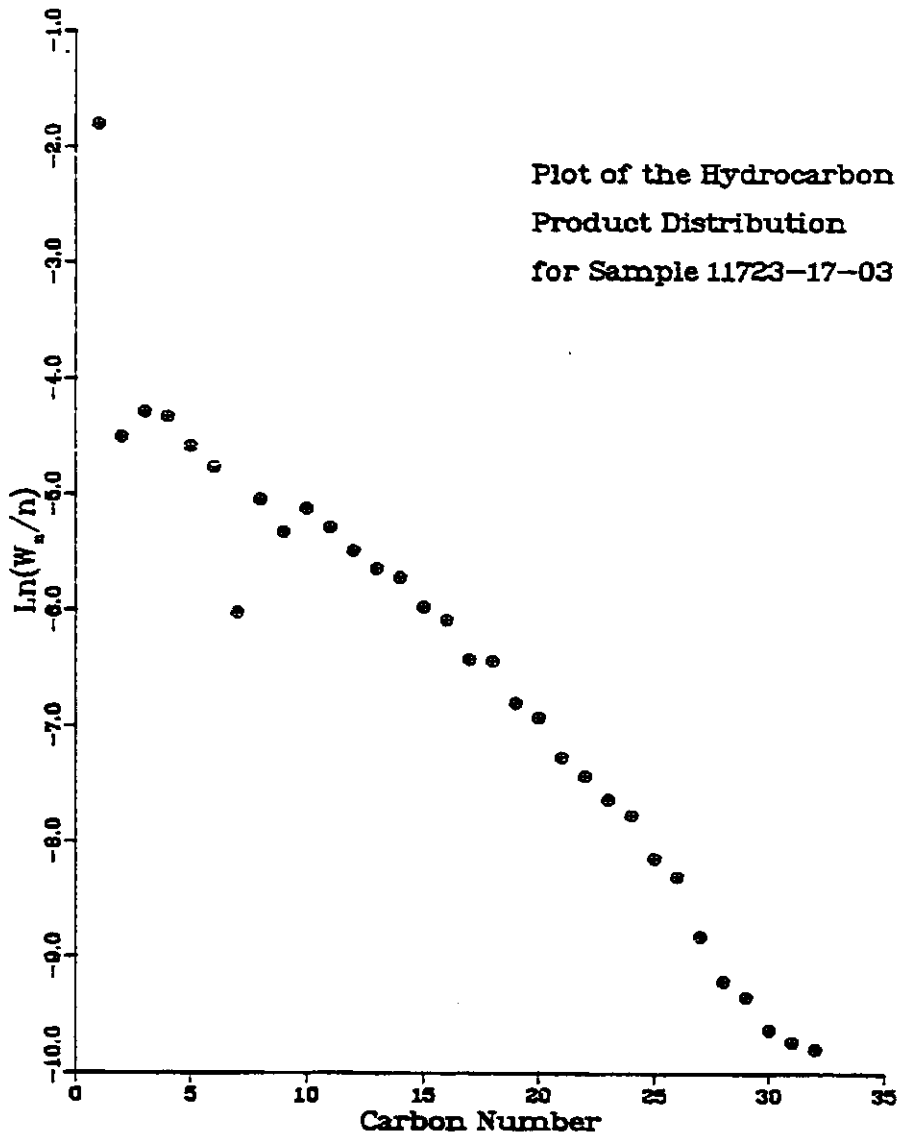


Fig. A12

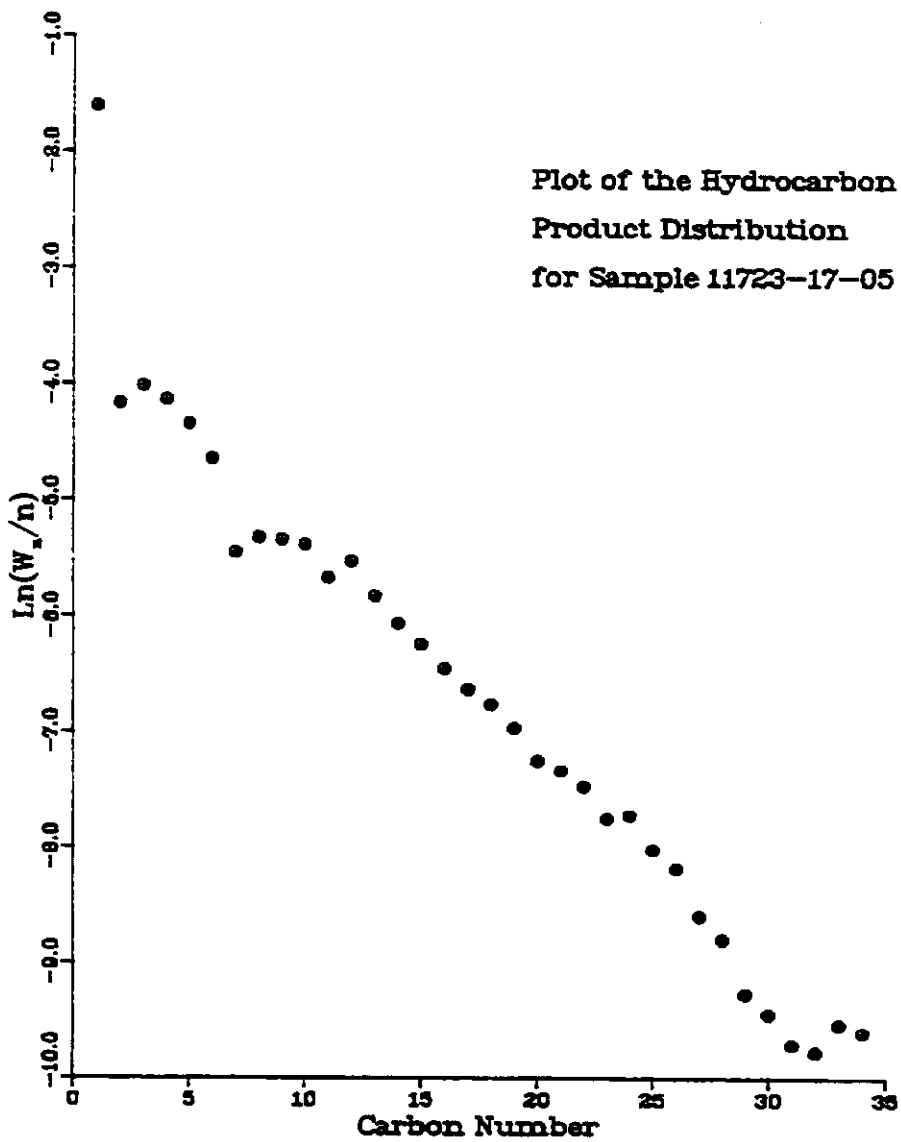


Fig. A13

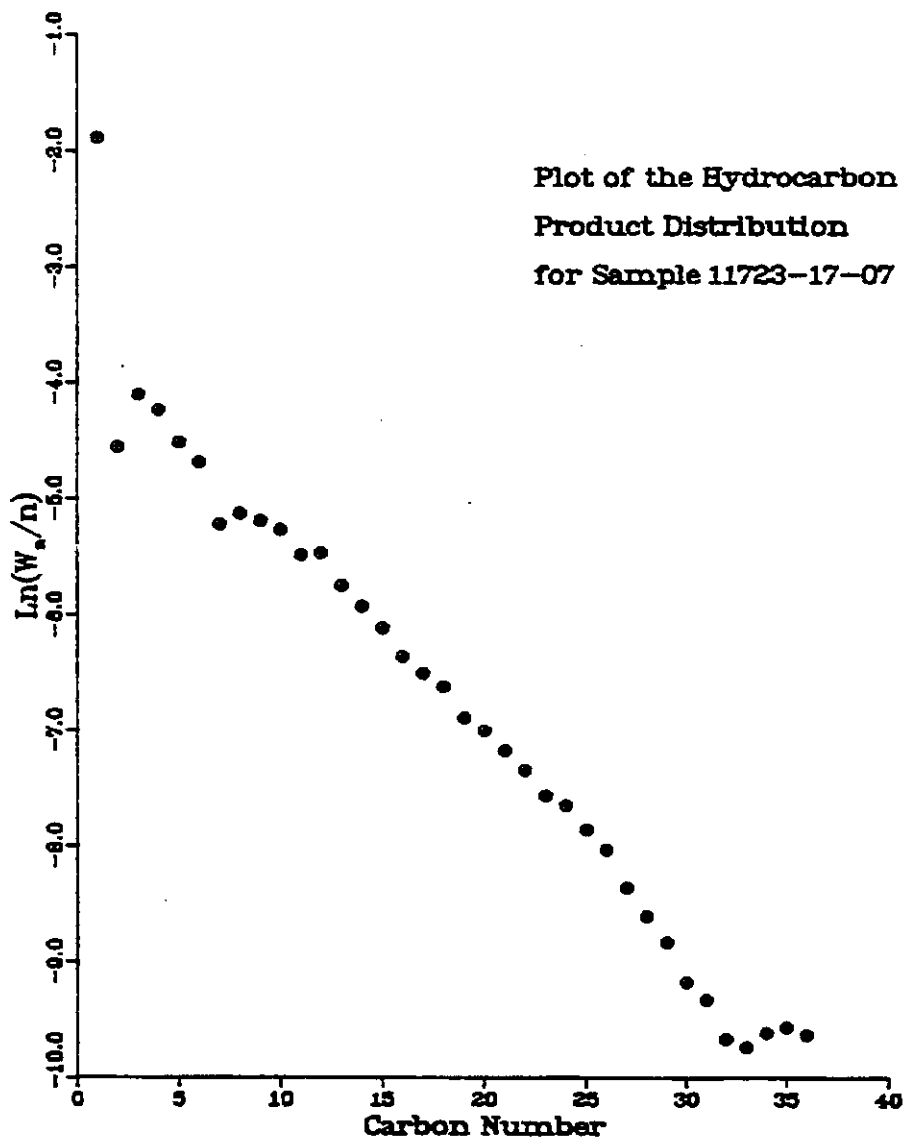


Fig. A14

