

APPENDIX B. CATALYST TESTING: DETAILS OF RUNS
INITIALLY REPORTED DURING LAST QUARTER

APPENDIX B. CATALYST TESTING: DETAILS OF RUNS
INITIALLY REPORTED DURING LAST QUARTER

J. G. Miller, L. F. Elek, C-L Yang and K. N. Beale

Contents

I. Introduction	B3
II. Run 44 (12561-01) with Catalyst 44 (Co/X ₉ /X ₁₀ /TC-103)	B4
III. Run 45 (12570-02) with Catalyst 45 (Co/X ₁₁ /TC-123)	B32
IV. Run 46 (12561-02) with Catalyst 46 (Co/X ₁₁ /TC-133)	B131
V. Run 47 (11617-06) with Catalyst 47 (Co/X ₉ /X ₁₀ /TC-103)	B176
VI. Run 48 (11617-07) with Catalyst 48 (Co/X ₁₁ /X ₁₂ /TC-123)	B186
VII. Summary	B227

I. INTRODUCTION

Presented in this report are detailed analyses of the five catalyst test runs summarized in Appendix A of the Fifth Quarterly Report, which constituted the major thrust of the work during that quarter.

All five catalysts were formulated by the method first used with Catalyst 11 (Run 12185-07) of the Third Quarterly Report. Three different catalyst supports were tested: TC-103, the most effective Molecular Sieve developed to date, and two newly developed supports, TC-123 and TC-133.

Two of the catalysts contained X_{11} -promoted cobalt oxide in contact with the Molecular Sieve, one contained the promoters X_{11} and X_{12} , and two contained the promoters X_9 and X_{10} .

The purpose of the two tests with X_9 and X_{10} was to investigate potential deviations from the carbon number cut-off characteristic of standard Schulz-Flory kinetics. The three others were attempts to improve on the superior performance of Catalyst 32 (Co/ X_{11} /TC-103, Run 12200-19). Variations on additives and catalyst supports were examined.

II. Run 44 (12561-01) with Catalyst 44 (Co/X₉/X₁₀/TC-103)

This run was an attempt to replicate the product selectivity obtained in Run 20, which deviated from standard Schulz-Flory kinetics in showing a carbon number cut-off after about C₂₅, the heavy end of the diesel range. The catalyst contained cobalt oxide promoted with X₉ and X₁₀, and was formulated by the same method as Catalyst 20.

Conversion, product selectivity, isomerization of the pentane, and percent olefins of the C₄'s are plotted against time on stream in Figs. B1-4. Simulated distillations of the C₅⁺ product are plotted in Figs. B5-10. Carbon number product distributions are plotted in Figs. B11-16. Chromatograms from simulated distillations are reproduced in Figs. B17-22. Detailed material balances appear in Tables B1-2.

The conditions of the run were the same as with Catalyst 20 with one difference: the reaction temperature was reduced to 240C in an attempt to prevent the extensive deactivation found with Catalyst 20 at 260C.

The initial syngas conversion was 48 percent, far below the 88 percent obtained with Catalyst 20. The initial water gas shift activity, with only five percent of the oxygen converted to CO₂, was also far lower than the 60 percent conversion with Catalyst 20; this effect has been found in earlier runs with the

same type of catalyst at 240C.

The test was run for 235 hours to make certain that the reactor system had reached equilibrium. Once a good material balance had been obtained (Samples 4-8), the Schulz-Flory plots showed no significant deviation from standard Schulz-Flory kinetics; except for the usual excess of methane, the plots were linear, lacking any suggestion of a carbon number cut-off like the one obtained with Catalyst 20.

Either the carbon number cut-off of Catalyst 20 was an artifact due to high initial deactivation, or its failure to appear in this run was due to the lower reaction temperature.

RUN 12561-01

1:1 H₂:CO
300 PSIG
240°C

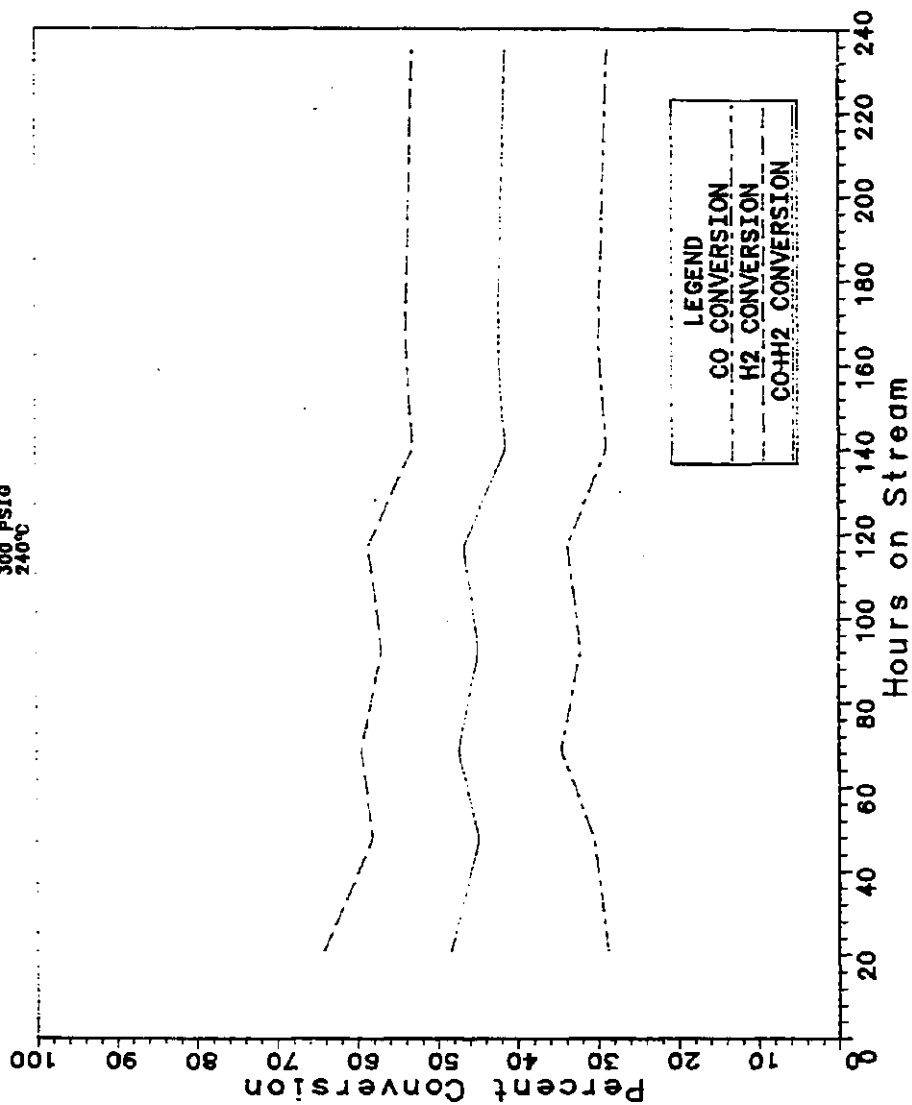


Fig. B1

RUN 12561-01

1:1 H₂:CO
300 PSIG
240°C

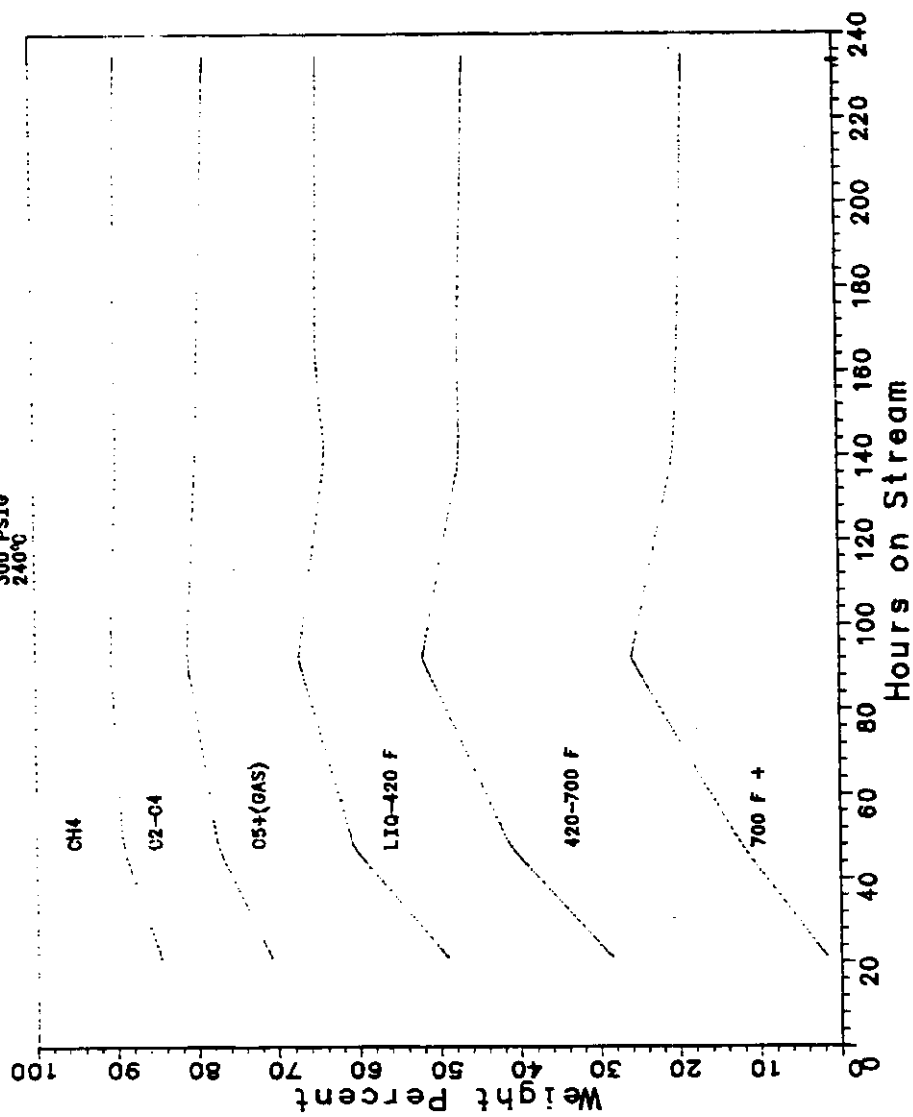


Fig. B2

RUN 12561-01

1:1 H2:CO
300 PSIG
240°C

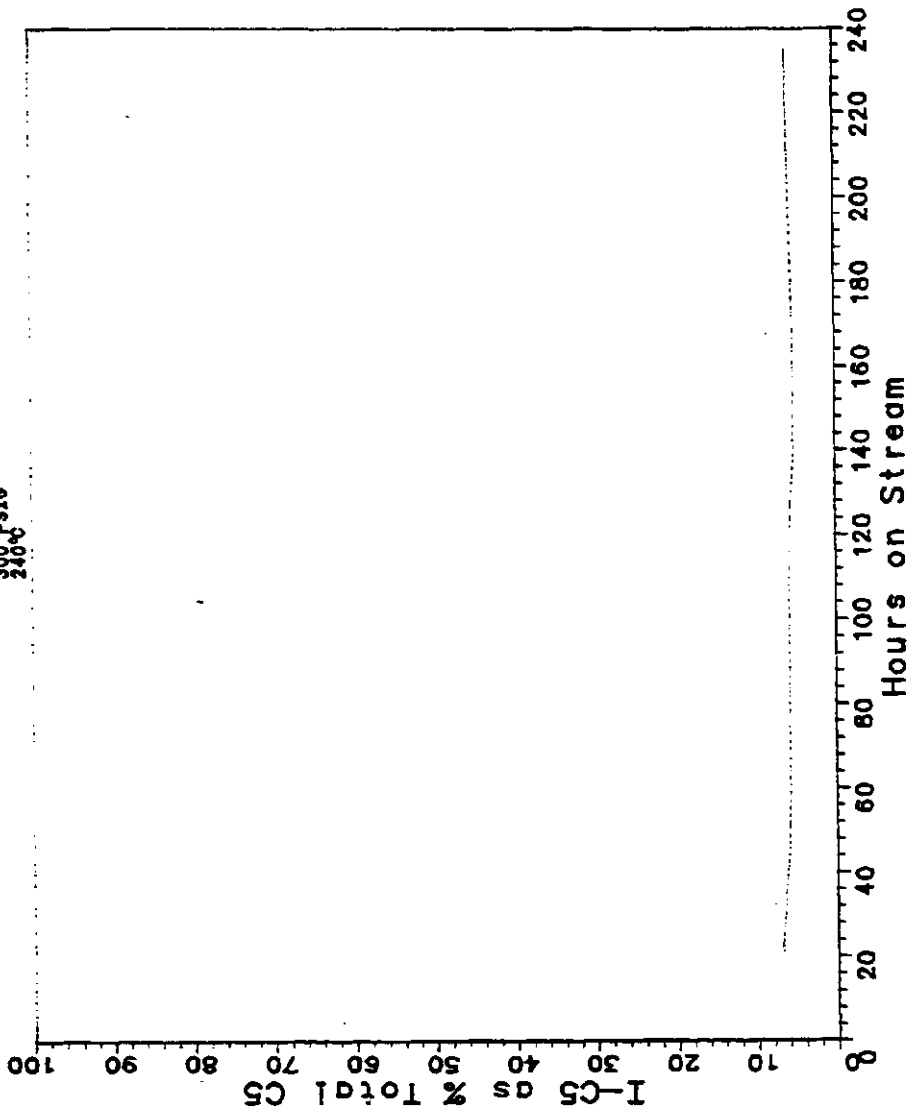


Fig. B3

RUN 12561-01

1:1 H₂:CO
300 PSIG
240°C

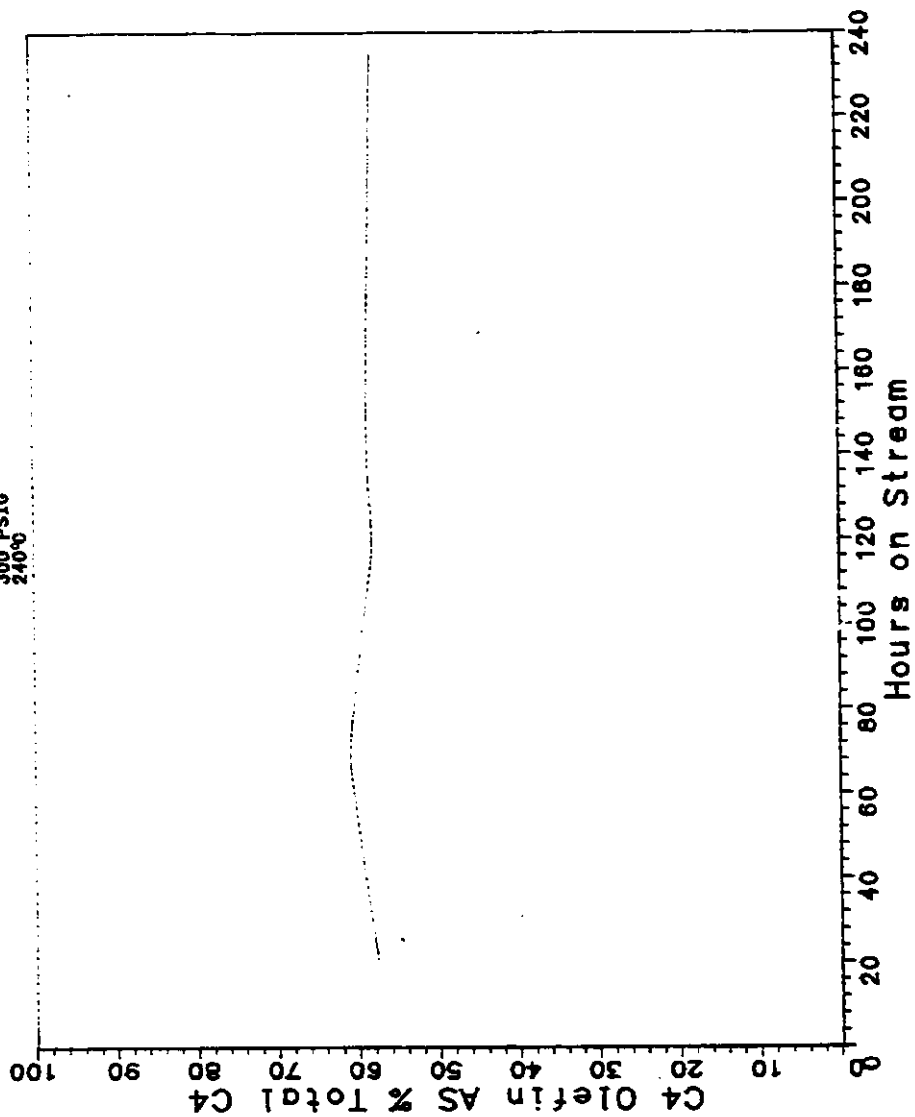


Fig. B4

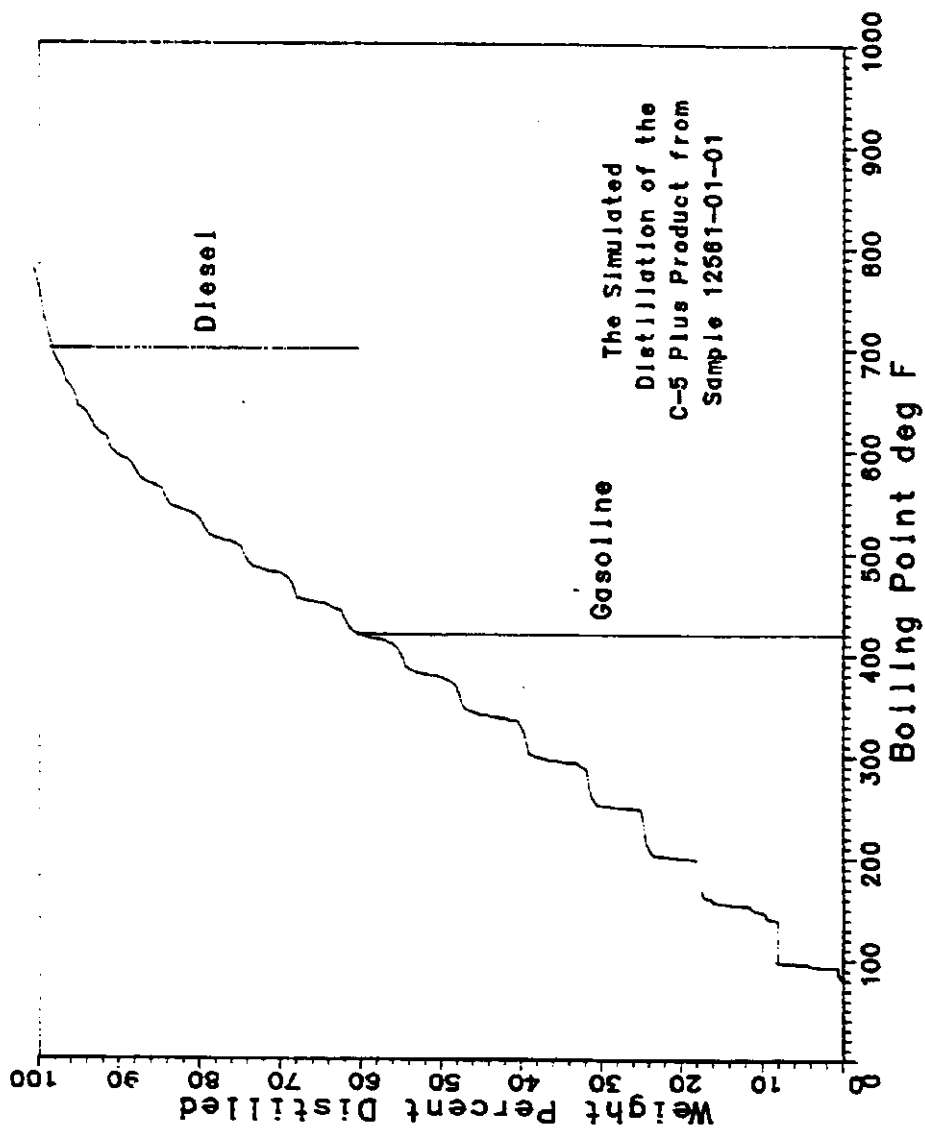


Fig. B5

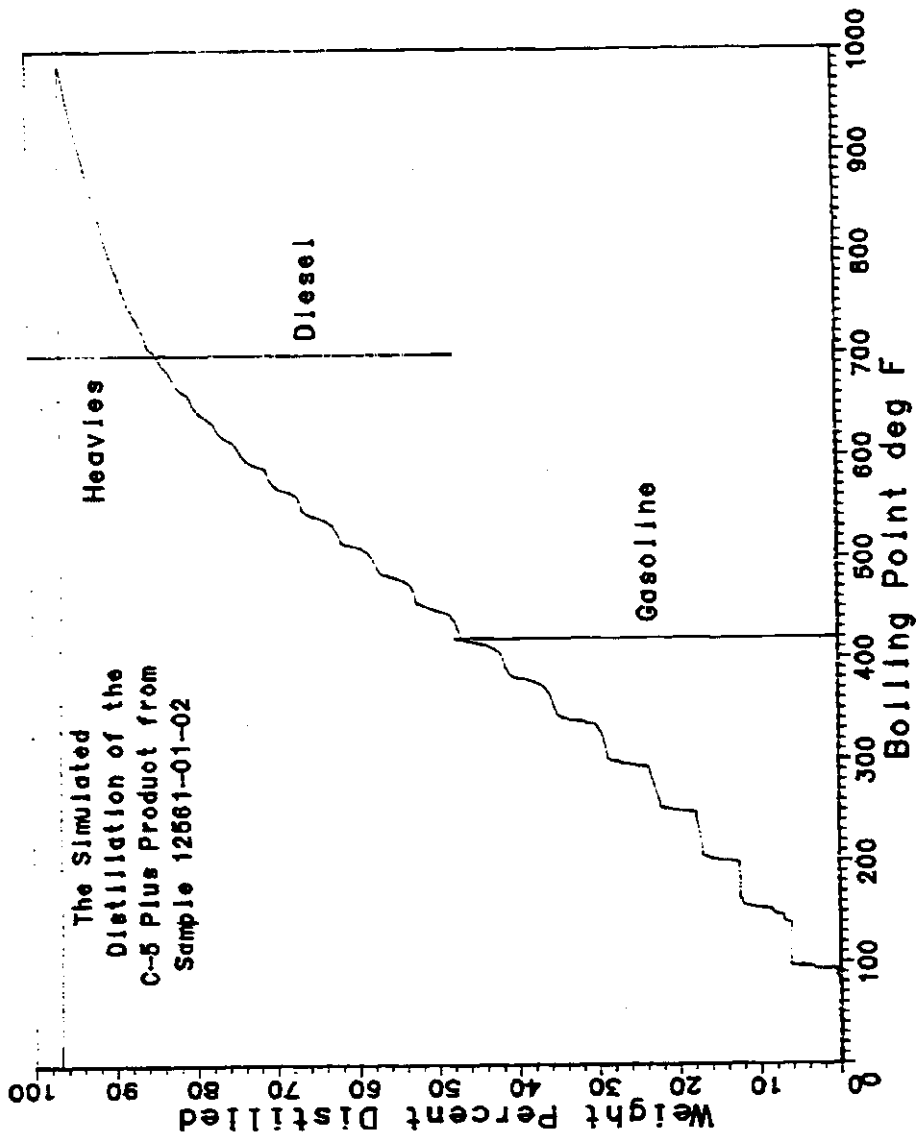


Fig. B6

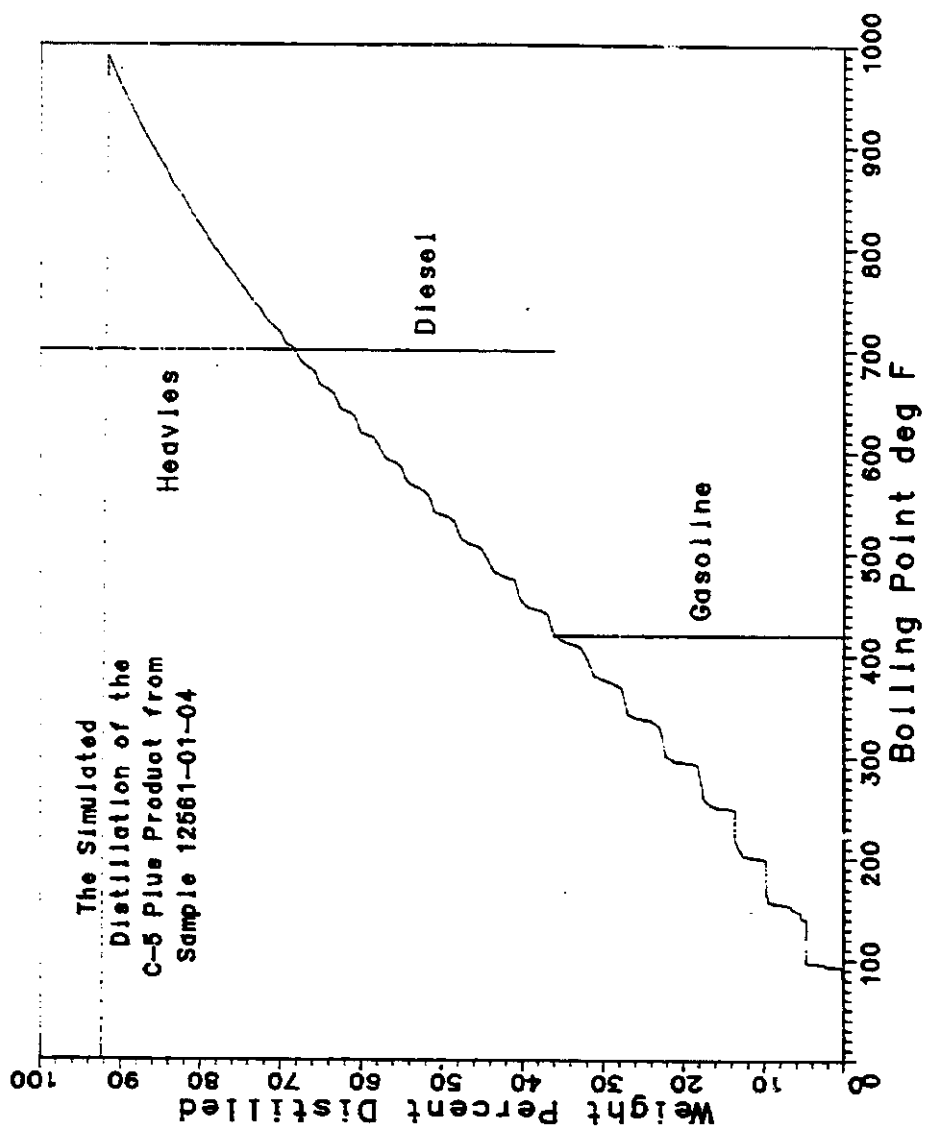


Fig. B7

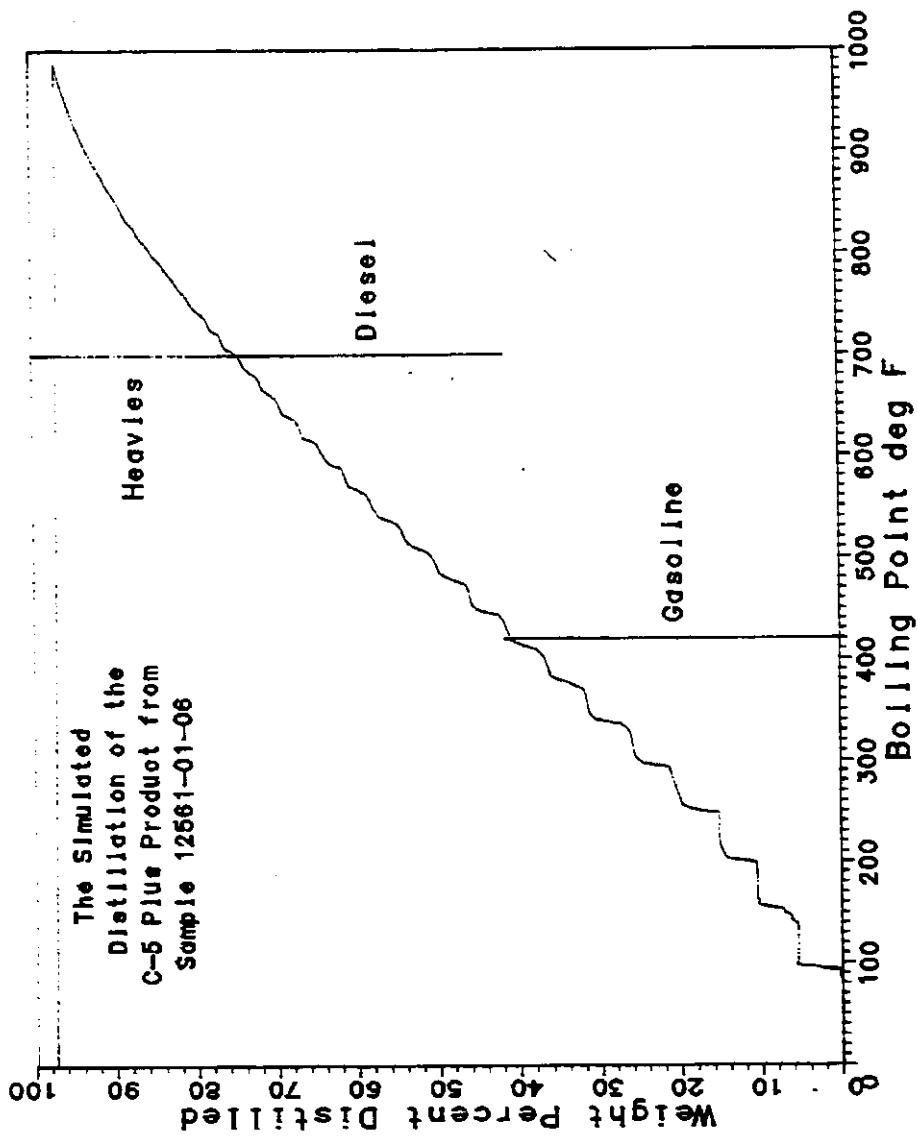


Fig. B8

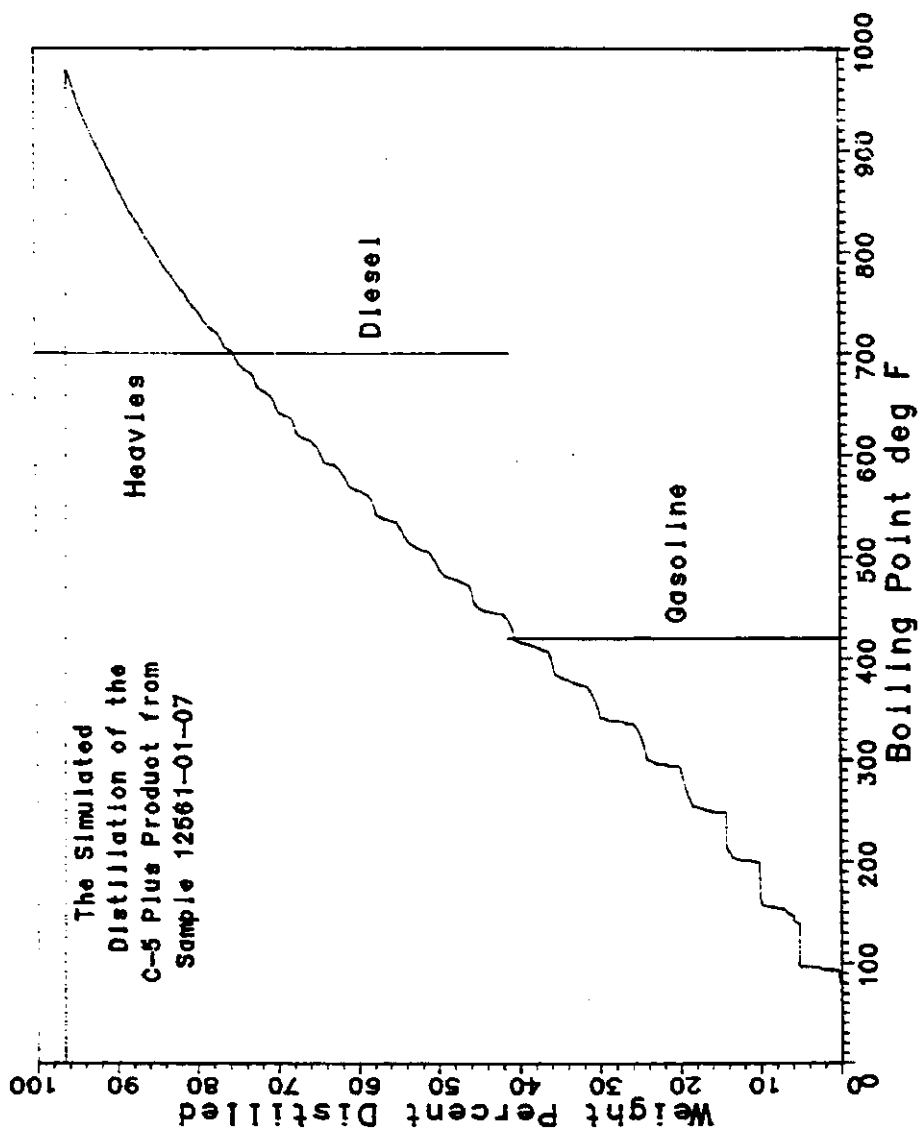


Fig. B9

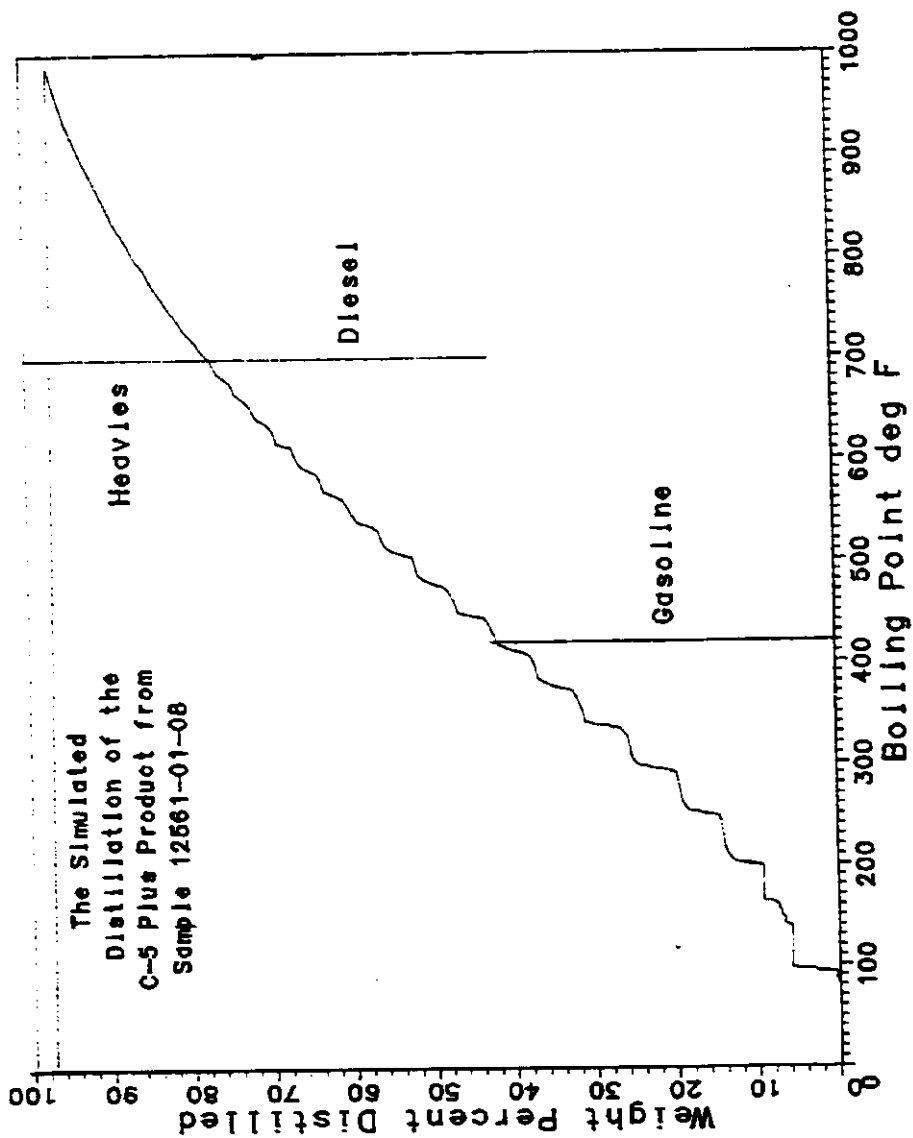


Fig. B10

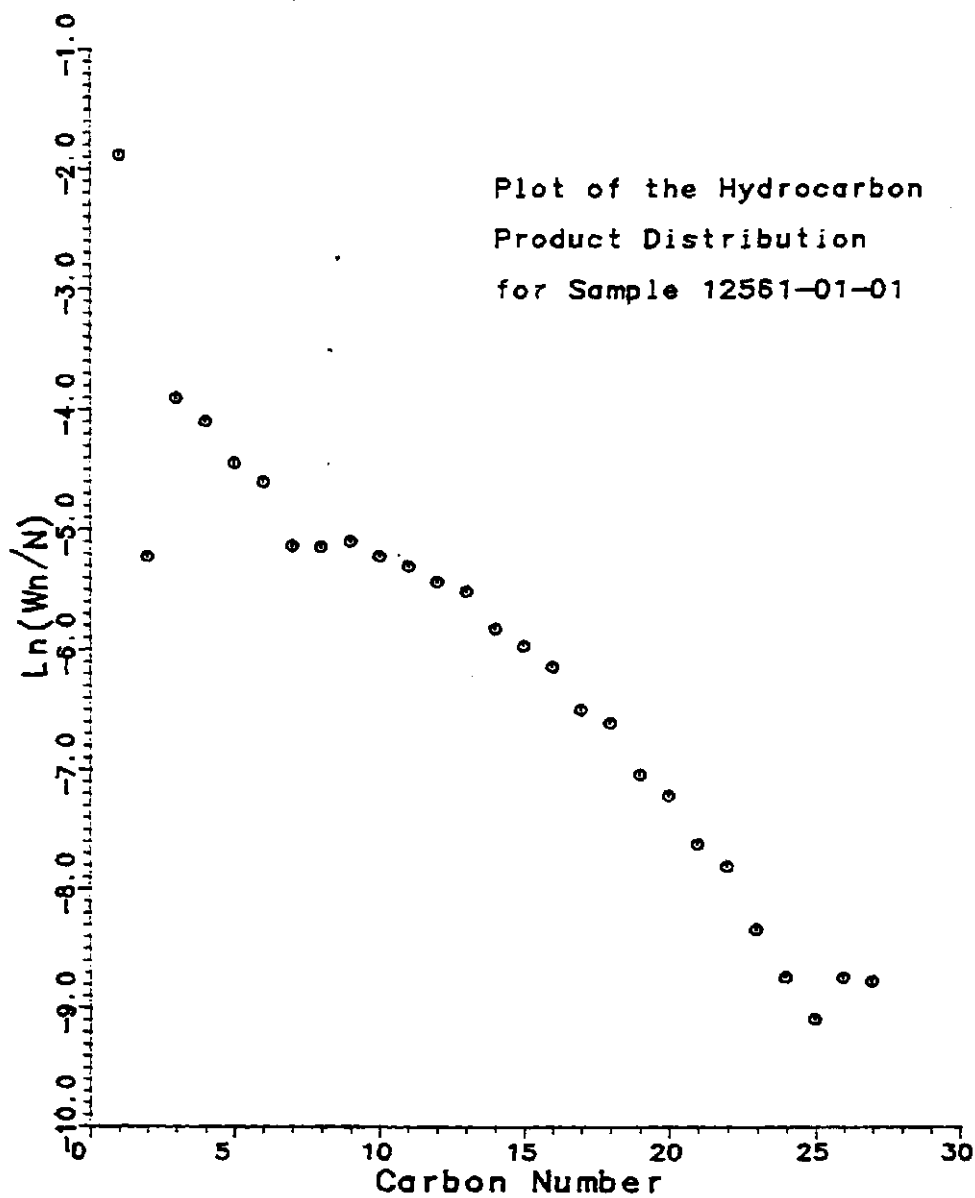
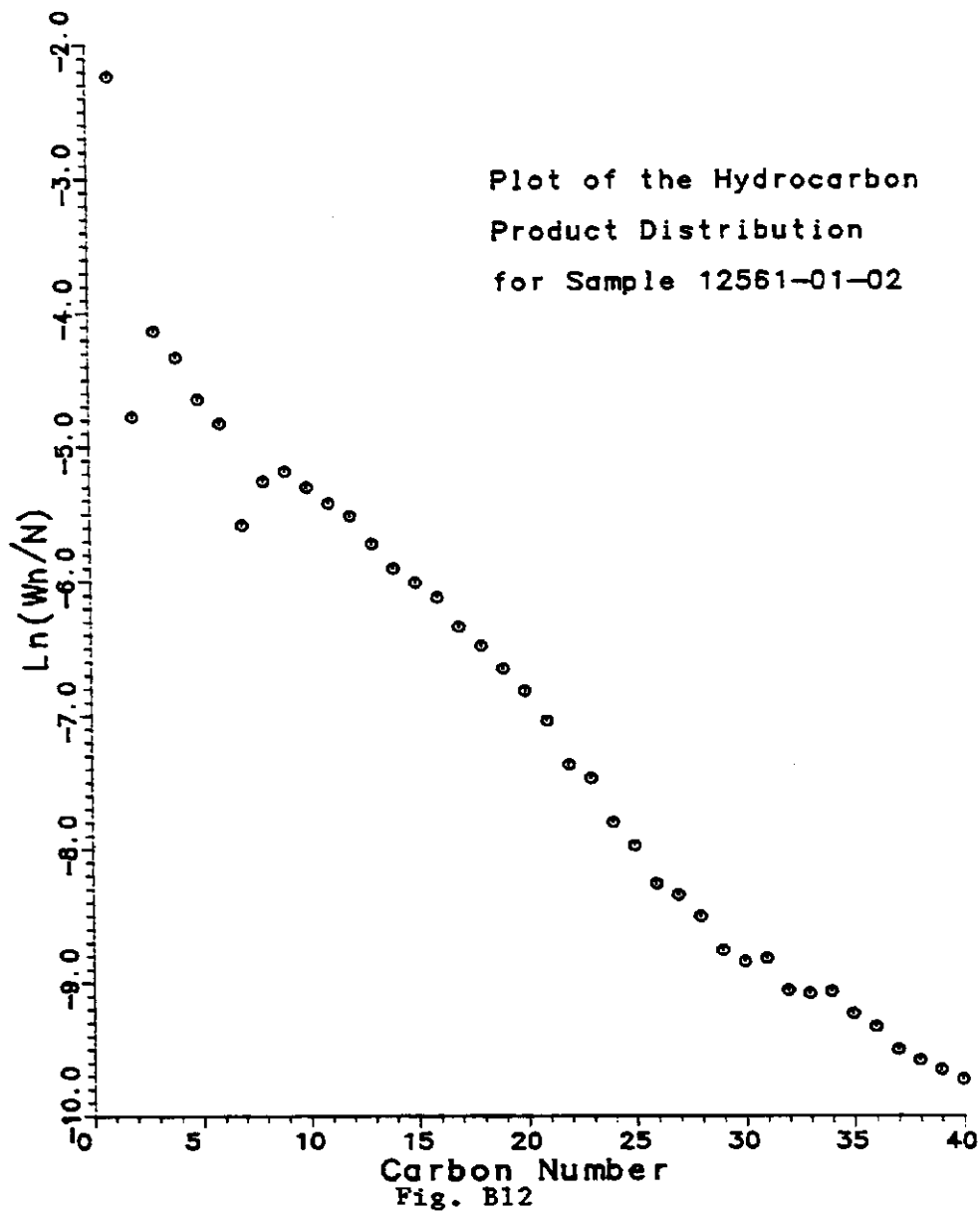


Fig. B11



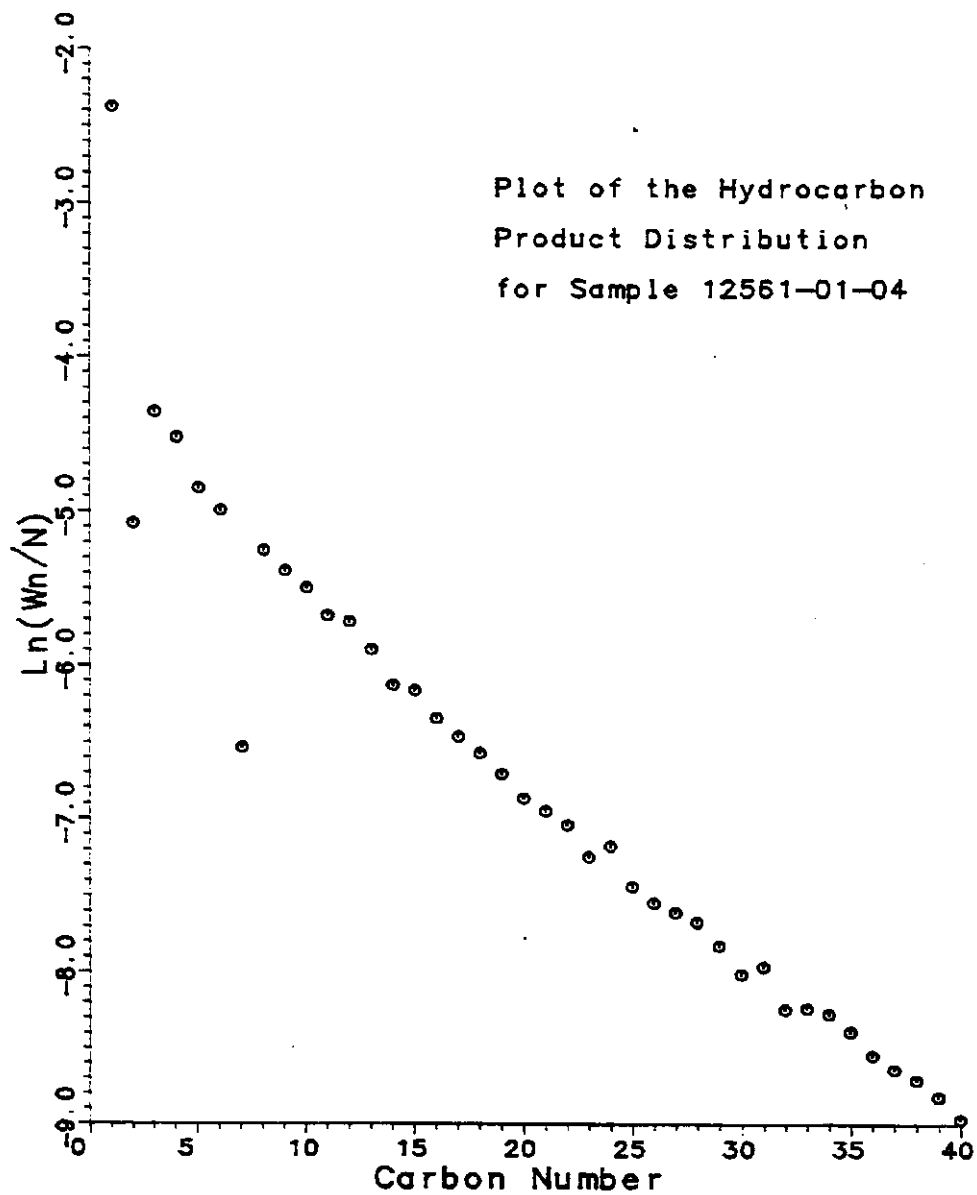


Fig. B13

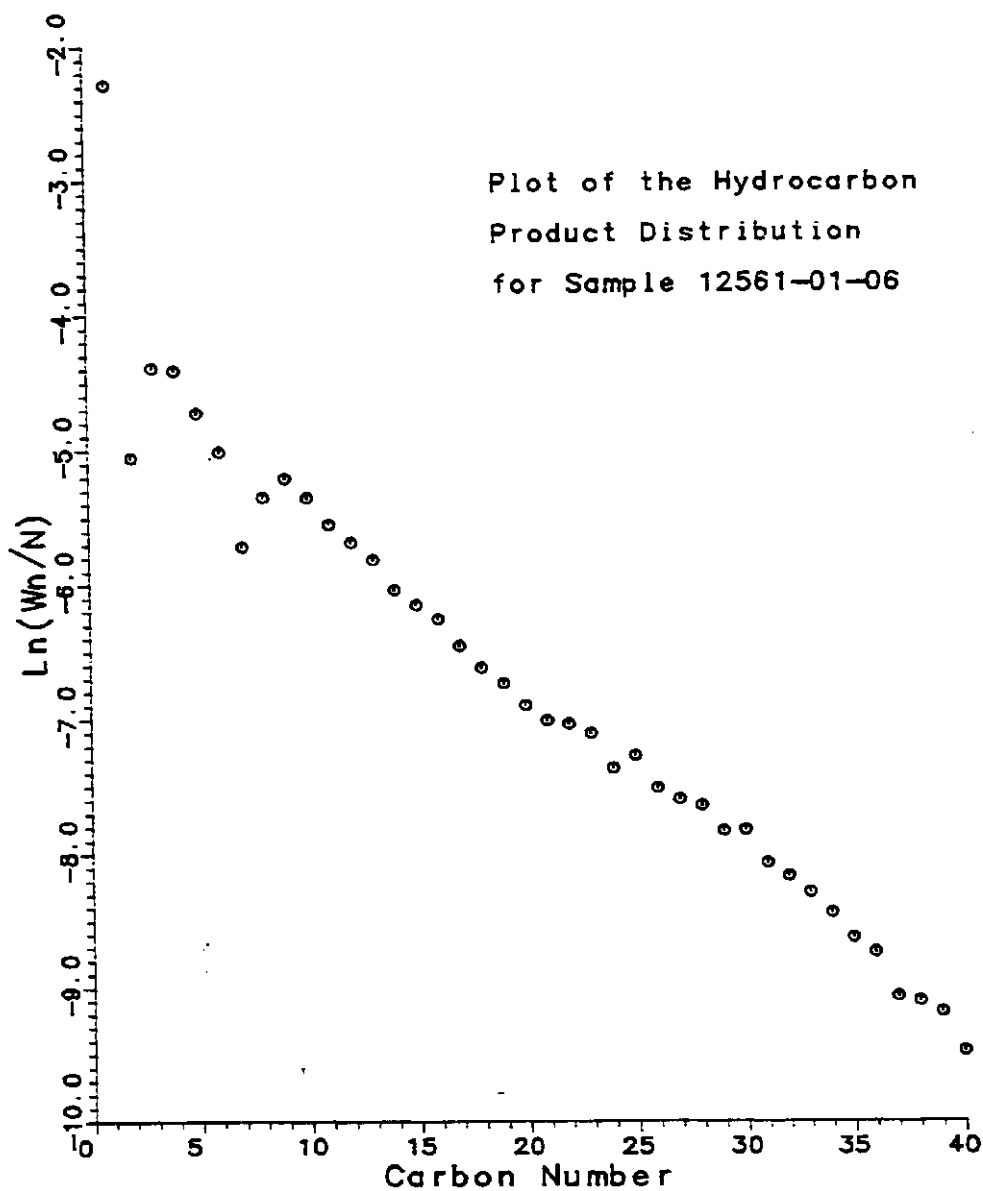


Fig. B14

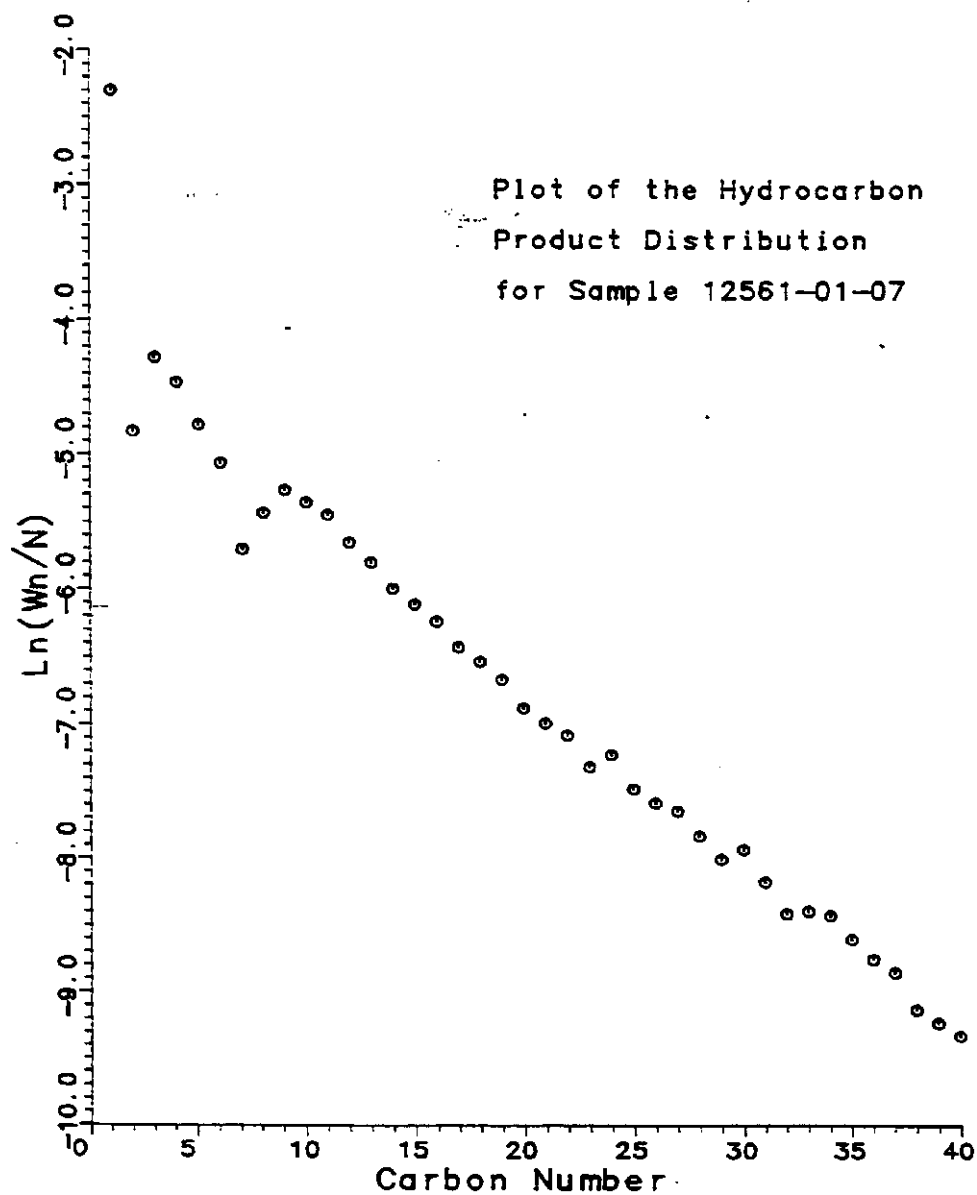


Fig. B15

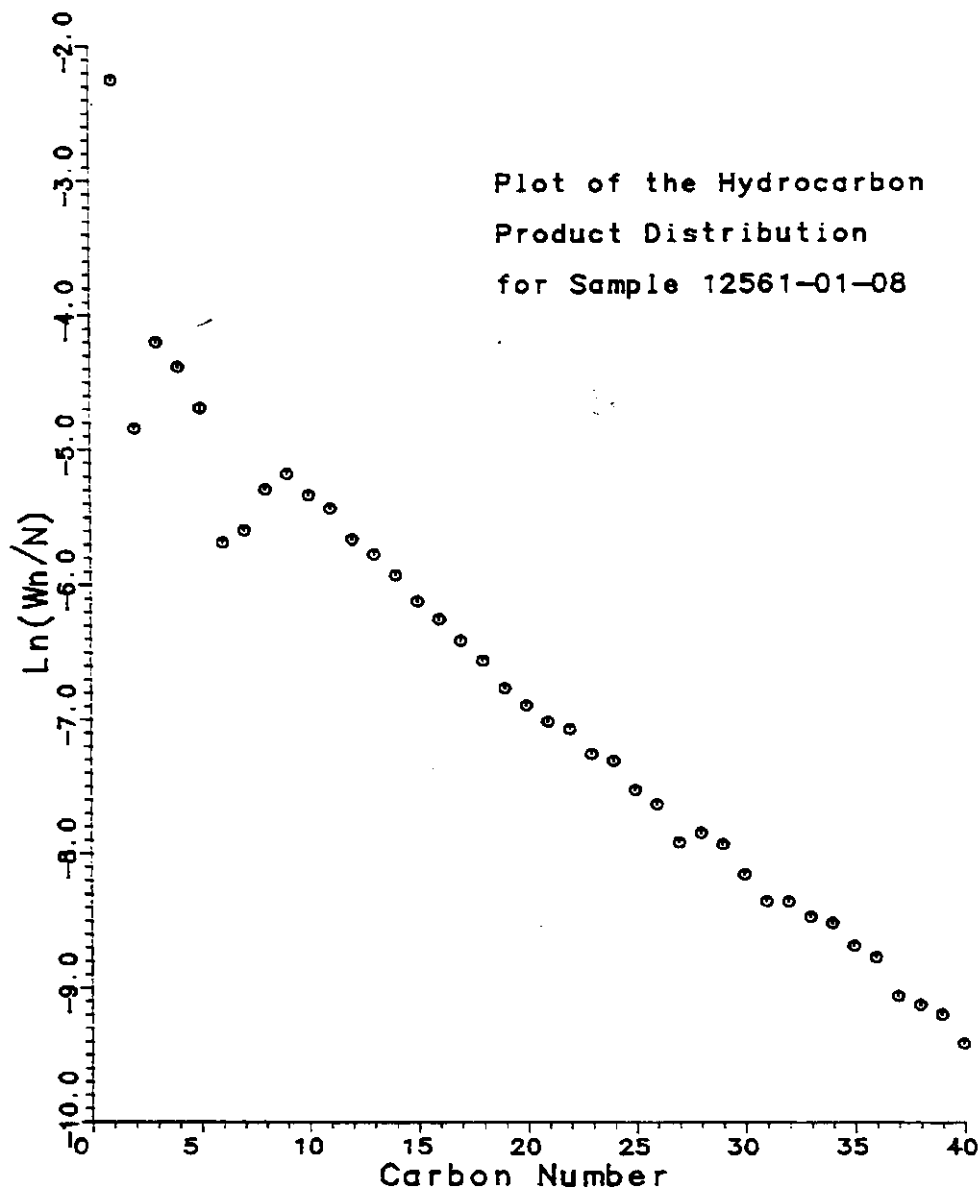


Fig. B16

017

OVEN TEMP NOT READY

PT: 111022 8.38

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=435°C

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=435°C

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=435°C

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=435°C

PT: OVEN TEMP=320°C SETPT=320°C LIMIT=435°C

PT: STOP RUN

PT: 111022 8.38

Fig. B17

OVEN TEMP NOT READY

111

ST: 511223 4.36

ST: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C

ST: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C

ST: OVEN TEMP=320°C SETPT=320°C LIMIT=405°C

ST: OVEN TEMP=400°C SETPT=400°C LIMIT=405°C

END 511223 4.36

511223-01-22

Fig. B18

- B23 -

07: LINES 0.28

01: OVER TEMP=320°C SETPT=320°C LIMIT=405°C

02: OVER TEMP=320°C SETPT=320°C LIMIT=405°C

03: OVER TEMP=320°C SETPT=320°C LIMIT=405°C

04: STOP RUN

Fig. B19