

V. Task 2 - Scoping Studies of Fischer-Tropsch Reactor-Wax Upgrading

A. Reactor-Wax Vacuum Fractionation

The F-T reactor-waxes normally contain a small amounts of catalyst fines when removed from the slurry reactor. This may make it unsuitable as a feedstock for some catalytic upgrading processes since the fines may foul the catalytic bed. One of the techniques to obtain a solids-free wax stream is to vacuum distill the reactor wax and then thermally crack the bottom fraction. The thermally cracked material can be recycled to the vacuum distillation tower. By this means, the solids-free overhead fraction becomes an excellent feedstock for further upgrading.

A scoping vacuum fractionation of a reactor-wax was conducted. A 10 kg sample of reactor-wax from Run CT-258-4 was fractionated using a laboratory vacuum distillation apparatus. The reactor-wax contained about 0.1-0.18 wt % of catalyst fines. The vacuum fractionation was prematurely terminated when a small amount of wax was found on the condenser. This happened when the cooling water temperature in the condenser was raised to the maximum (66°C). Also, a gradual vacuum loss (pressure increased from 0.5 to 1.2 mm Hg) was experienced. This vacuum loss might indicate some cracking of the reactor-wax during fractionation.

The distillation cut temperature at the termination of fractionation was 461°C. The different fractions collected during the distillation were:

<u>Fraction</u>	<u>Wt % (No Loss Basis)</u>
216°C-	0.02
216-343°C	1.13
343-399°C	2.53
399-454°C	6.95
454-461°C	6.31
461°C+ (Bottoms)	<u>83.06</u>
	100.00

The total recovery of the material after fractionation was 98.9 wt %. The overhead fractions were very clear and did not contain any catalyst fines. The bottom fraction (461°C+) was analyzed

for solid content and was found to contain about 0.11-0.16 wt % catalyst. A small amount of catalyst may have been left behind in the still. Overall, both the reactor-wax and the catalyst balances were good.

The laboratory distillation apparatus, which is widely used in the vacuum fractionation of conventional petroleum wax, could not simulate the commercial vacuum fractionation of the reactor-wax, since a 566°C cut point can generally be achieved in commercial vacuum fractionation towers. The limitation of the condenser temperature (maximum of 66°C) can be eliminated only by expensive modification of the distillation apparatus. Another way to estimate the fraction of vacuum separations is to use the carbon-number distribution of the distillation apparatus. Another carbon-number distribution of the reactor-wax. The 566°C cut point is roughly equivalent to a paraffin of forty-seven carbon-number. Based on this equivalence, one can expect that about 30 wt % of the Run CT-256-4 reactor-wax sample shall become an overhead fraction in a commercial vacuum fractionation tower.

B. Thermal Cracking of a Fischer-Tropsch Reactor-Wax Vacuum Bottom

As mentioned in the preceding Section, the objective of F-T reactor-wax thermal cracking is to obtain solid-free waxes (of about 566°C⁻) for further upgrading. Altogether, five scoping batch runs were made using a laboratory "shaker bomb" setup. The experimental conditions are summarized in Table V-1.

The 481°C⁺ vacuum bottoms from the Run CT-256-4 reactor-wax was used as a feed for four runs carried out at 454°C with 400, 800, and 1,200 ERT severities. Here the ERT is the Equivalent Residence Time in the thermal cracker estimated at 427°C. However, in a commercial plant the feed used will be heavier (566°C⁺ = C₄₇⁺) since a higher vacuum separation endpoint can be achieved there. Hence, we tried to obtain an as high a vacuum separation cutpoint as possible. Using a small analytical vacuum still we were able to obtain about 300 g of 503°C⁺ material which was used as feed in a 1,200 ERT severity run.

The liquid products were analyzed by the modified gas chromatography method used for heavy reactor-waxes (see Section VI.B). The gaseous products were very small in quantity and a representative sample could not be collected in sufficient quantity for analysis.

Figure V-1 shows the composition of products from thermal cracking of the 481°C⁺ feed and Figure V-2 summarizes the composition of products from the thermal cracking of 503°C⁺ feed. The conversion of interest is the conversion of C₄₇⁺ hydrocarbons (566°C⁺) into C₄₇⁻ products, since the vacuum distillation cutpoint is 566°C. Table V-2 summarizes the conversions achieved during all runs at various severities.

Table V-1

Thermal Cracking of a Fischer-Tropsch
Reactor-Wax Vacuum Bottom

Run No.	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Charge Cutpoint, °C	461 ⁺	461 ⁺	461 ⁺	461 ⁺	503 ⁺
Charge Weight, g	200	200	200	200	200
Temperature, °C	454	454	454	454	454
Run Time, s	162	77	162	250	250
ERT, s	800	400	800	1,200	1,200
Pressure, MPa	1.48	0.79	1.20	--	--
Liquid Product, g	195.3	195.9	186.5	197.1	196.9
Light Gas, NL	1.72	0.79	1.58	2.53	0.18
C ₄₇₊ Converted, wt %	18.0	11.2	39.9	37.4	45.6

Figure V-1
THERMAL CRACKING OF F-T REACTOR-WAX
 (RUN CT-256-4 WAX)

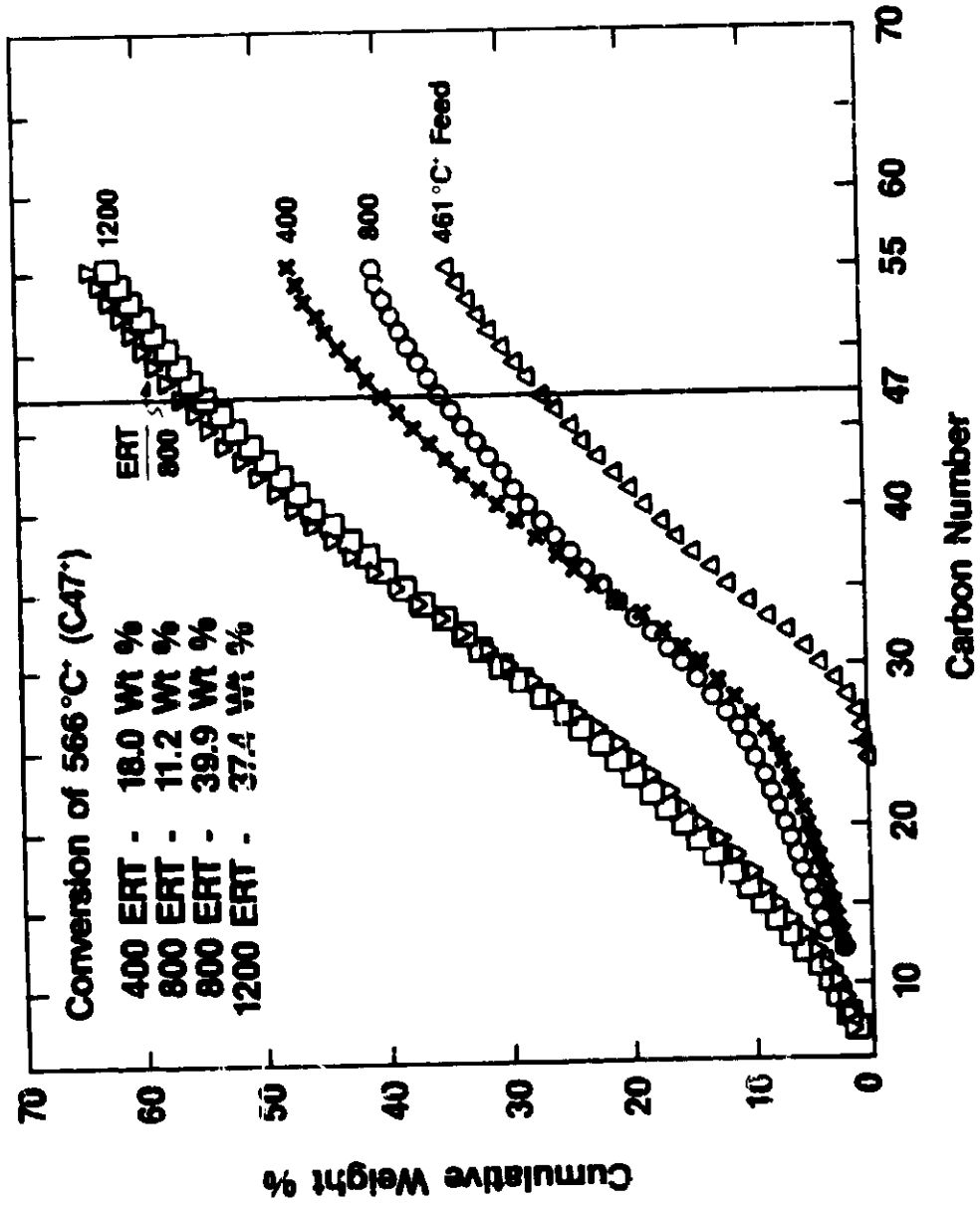


Figure V-2
THERMAL CRACKING OF F-T REACTOR-WAX

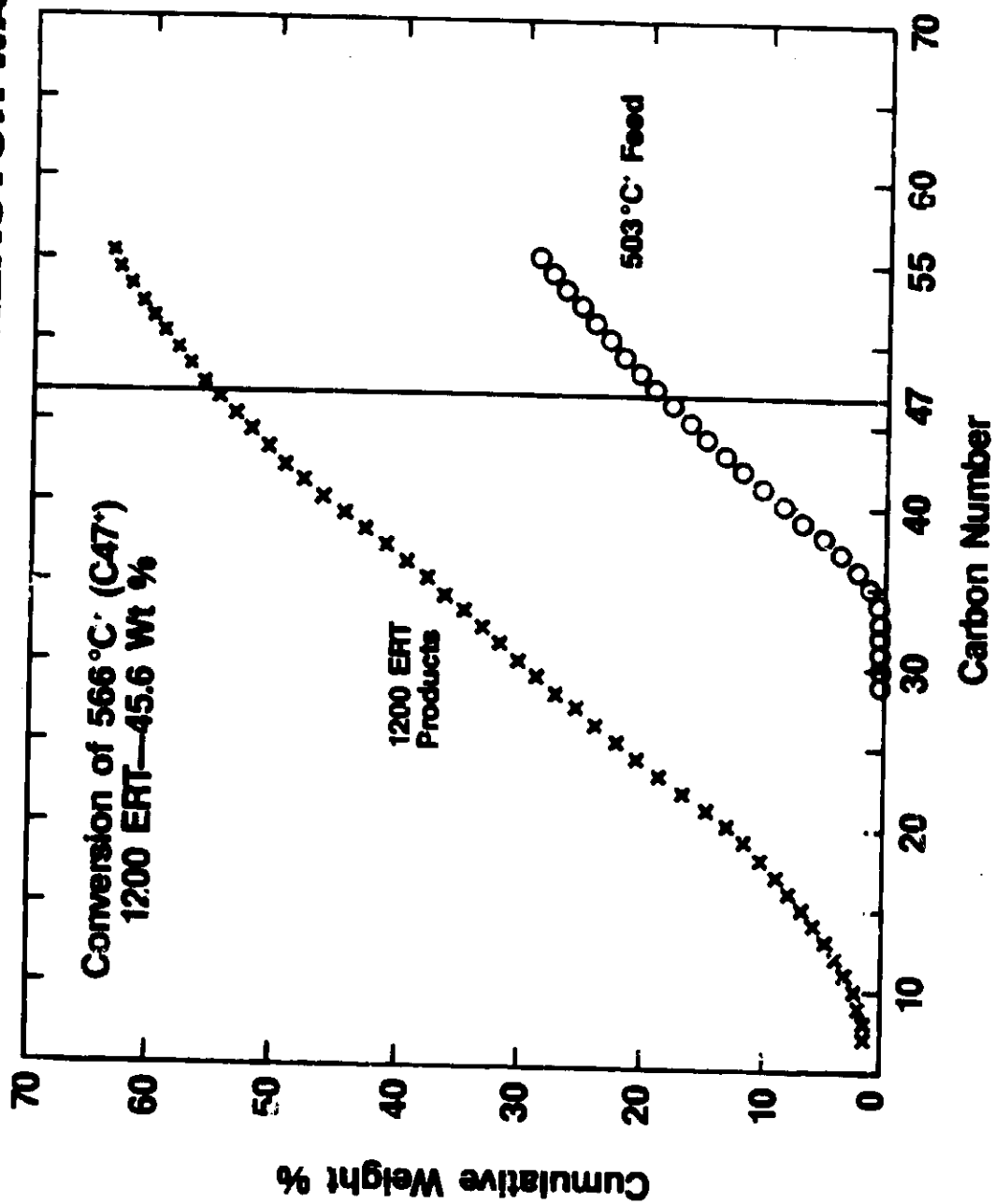


Table V-2

Thermal Cracking of a Fischer-Tropsch
Reactor-Wax Vacuum Bottom - Conversion

<u>Feed (Vacuum Bottom)</u>	<u>ERT, s</u>	<u>Conversion of C₄₇₊</u>
461°C+	400	18.0
461°C+	800	11.2 and 39.9
461°C+	1,200	37.4
503°C+	1,200	45.6

As seen from the results, the two 800 ERT runs gave widely different results. We probably could attribute this discrepancy to difficulty in carrying out these runs. Due to the very waxy materials involved in these runs, the unit was constantly plagued with plugging problems. Also, this type of feed was never run in the unit before. The results of 400 and 1,200 ERT runs are consistent with the increased severity and follow a first-order kinetics, as demonstrated in Figure V-3 which is a plot of $-\ln(1-\text{conversion})$ versus equivalent resident time. As seen in the figure the 800 ERT results are completely off the straight line (corresponding to first-order kinetics) fitted to the 800 and 1,200 ERT results. Also, conversion at 1,200 ERT using heavier feed improved from 37.4 to 45.6%.

These scoping runs have demonstrated that at least ~40% conversion of C_{47}^+ material can be achieved at 454°C and 1,200 ERT severity. The heavier material can be recycled back to the thermal cracker after a vacuum separation. A recycle ratio of 1.5 (based on fresh feed) will be required to achieve conversion of reactor-wax to extinction assuming that the heavier fraction has the same cracking characteristics as the fresh feed. Also, a small purge stream will be needed to prevent the accumulation of the small amount of catalyst present in the fresh feed. Using this method, it is expected that a solids-free C_{47}^- stream can be obtained for further processing.

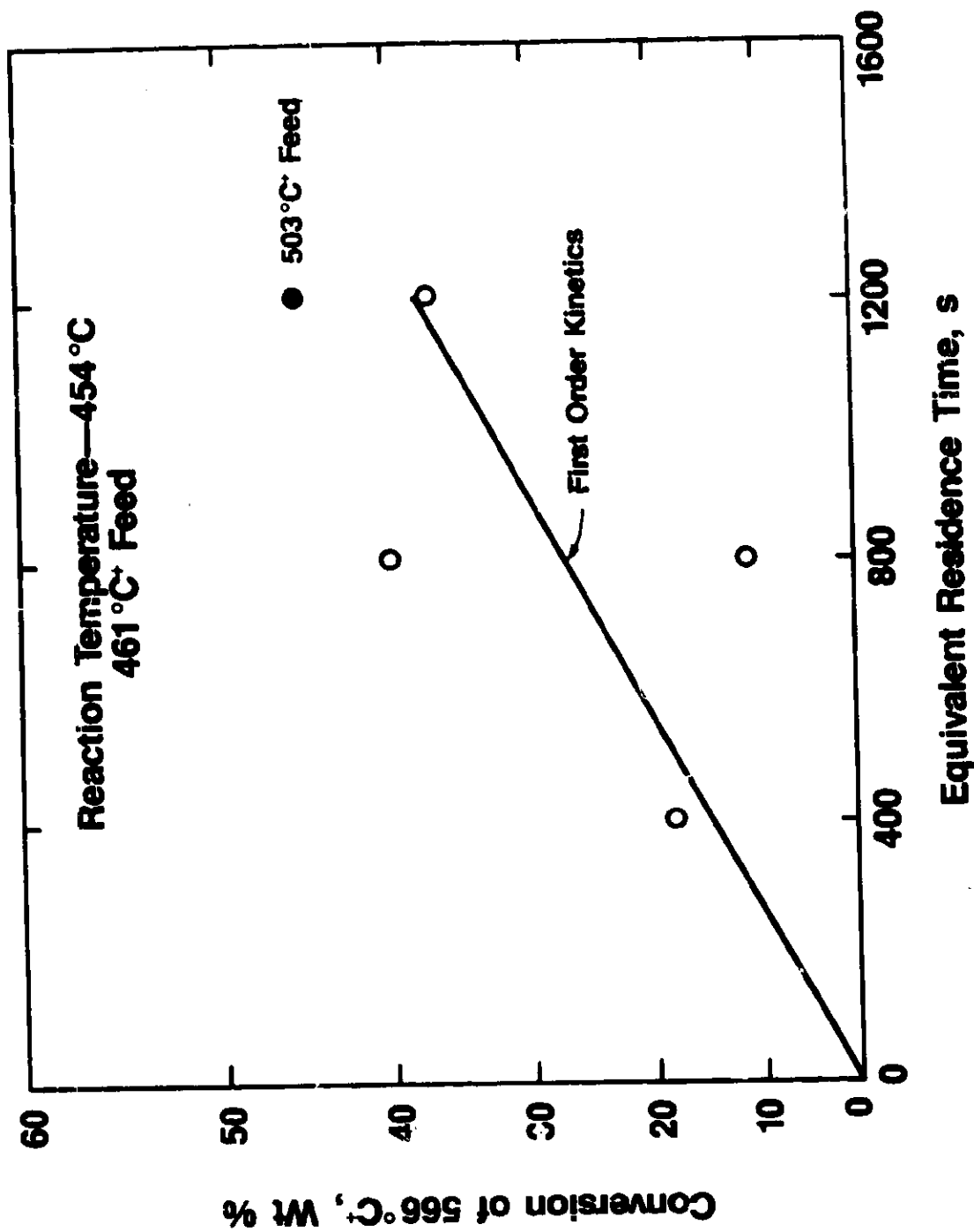
C. Other Scoping Studies

Other scoping reactor-wax upgrading studies, including:

- Testing of a High-Gradient Magnetic Separator for cleaning reactor-wax.
- Hydrodewaxing.
- Hydrocracking.
- Fluidized-Bed Catalytic Cracking

were carried out, and the results are reported in the Appendix-Restrictive Distribution.

Figure V-3
THERMAL CRACKING OF F-T REACTOR-WAX



VI. Task 3 Product Evaluation

A. Reactor-Wax Analyses by Gel Permeation Chromatography

We have evaluated a high temperature Gel Permeation Chromatography (GPC) method for F-T reactor-wax molecular weight distribution analysis. Two samples were submitted to a consulting analytical laboratory (Springborn Labs, Enfield, CT) for high temperature GPC which employed a standard column packing optimized for general polymer analysis. After reviewing the GPC data, we concluded that in order to obtain a correct reactor-wax molecular weight distribution, further optimization of the GPC column packings is required to improve the resolution. This would require column packings with smaller pore distribution. Since it is expensive to modify the column packings, we did not pursue this method any further.

B. Modified Gas Chromatography for Reactor-Wax Analyses

Based on the results of the vacuum-fractionation of Run CT-256-4 reactor-wax, it was shown that the reactor-wax contained a large fraction of hydrocarbons heavier than C₆₀. The gas chromatography (GC) method used to this point was limited to hydrocarbons up to C₆₀.

A modified gas chromatographic method was hence developed to obtain "boiling point" profiles (carbon number distribution) and to estimate the fraction of reactor-wax boiling above 596°C (C₅₅⁺). As described below, two major improvements were done to accomplish this.

A suitable solvent is not available to completely dissolve the heavy reactor-wax sample prior to injection into the GC. To circumvent the solubility problem, the reactor-wax was injected as solids by employing a packed, cool-on-column injection port. The second improvement was the addition of a small but known amount of n-C₁₁, n-C₁₂ and n-C₁₃ hydrocarbons as internal standards. These standards were used to prorate the amount of reactor-wax which was not eluted from the GC column (i.e., the C₅₅⁺ hydrocarbons). Figure VI-1 shows a typical chromatogram for Run CT-256-4 reactor-wax.

The reactor-waxes from Runs CT-256-3, -4, and -5 were reanalyzed by the improved method and the results are reported in the Table VI-1. Reactor-wax from Run CT-256-3, which gave a low yield of reactor-wax (4-30 wt % of total hydrocarbons), contained only 6 wt % of C₅₅⁺. This is consistent with the earlier

Figure VI-1
GAS CHROMATOGRAM OF RUN CT-256-4 REACTOR-WAX

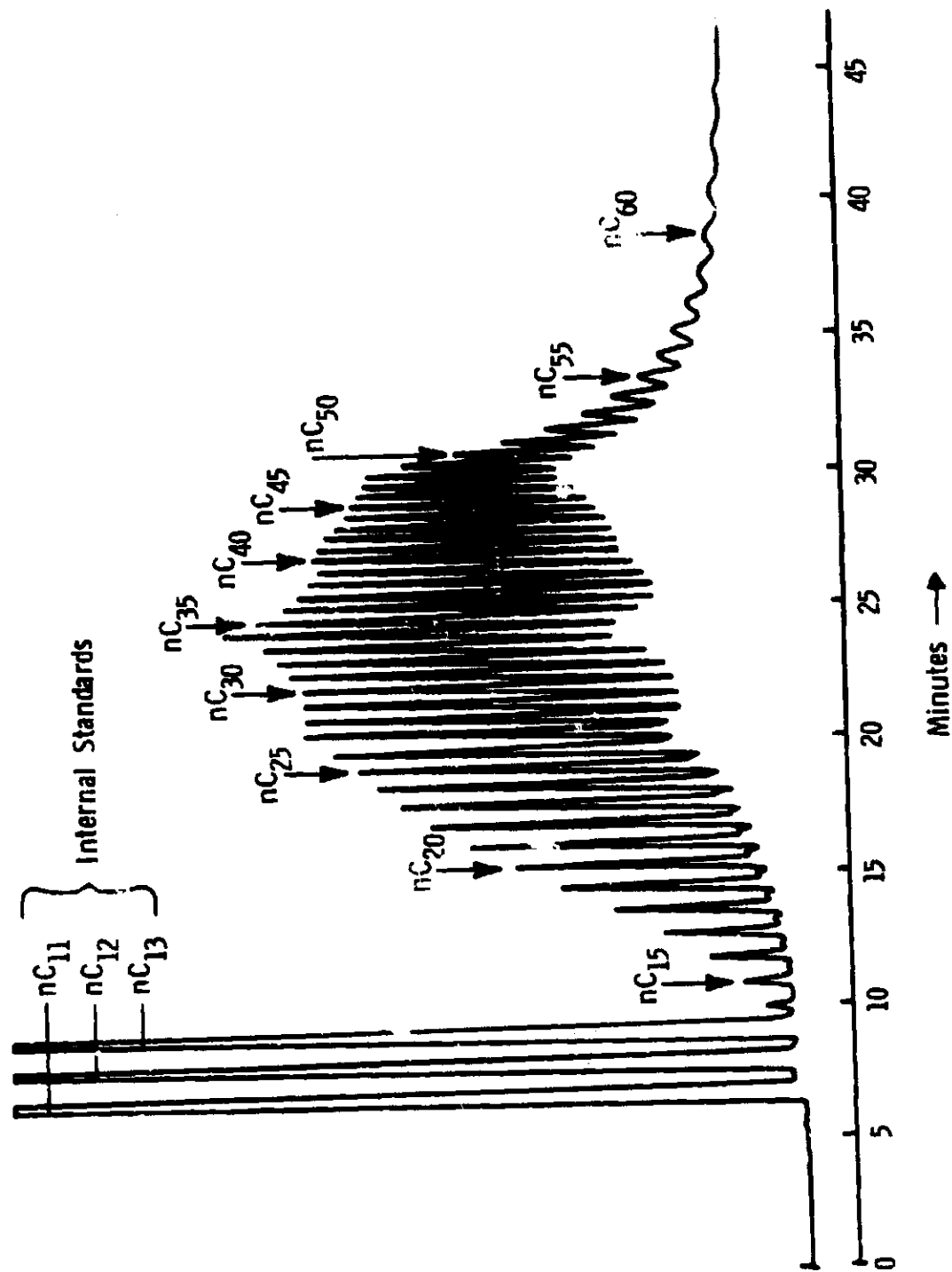


Table VI-1
 Composition of
Fischer-Tropsch Reactor-Waxes

<u>Carbon Number</u>	<u>Run CT-256-3</u>	<u>Run CT-256-4</u>	<u>Run CT-256-5</u>
10-20	7.7	1.9	1.5
21-25	15.1	3.9	3.1
26-30	19.8	6.2	3.9
31-35	17.9	6.6	4.3
36-40	13.2	5.3	3.5
41-45	9.7	4.6	3.3
46-50	6.7	4.1	3.1
51-55	3.9	2.6	2.6
55+	<u>6.0</u>	<u>64.8</u>	<u>74.7</u>
Total	100.0	100.0	100.0

Unit: Wt %

analysis using the older GC method without internal standards. On the other hand, the reactor-waxes from Runs CT-256-4 and -5 (the high reactor-wax yield operation) contained 64.8 and 74.8 wt % of C₅₅⁺ hydrocarbons, respectively.

Table VI-2 compares the results from the improved GC analysis with those from the vacuum fractionation and shows the good agreement between them.

In view of the above results, it is interesting to compare the Schulz-Flory distribution (Flory, 1967) of Run CT-256-3 (Figure 21, Kuo, 1983) with that of Runs CT-256-4 and -5 (Figures VI-2 and -3). In all cases there is a distinct break in the slope at C₂₀, coinciding approximately with the inclusion of the reactor-wax. In addition, another break in the slope occurs for Runs CT-256-4 and -5 at C₆. Such a break was not observed with Run CT-256-3 data. As expected, the probability of chain growth for the C₂₀⁺ fraction increases from Run 3 to 4 to 5, i.e., with increasing wax yield and/or increasing molecular weight of the wax.

A possible explanation for the break in the Schultz-Flory distribution is the readsorption of large molecules on the catalyst active sites which results in further chain-growth.

C. Field Ionization Mass Spectrometry for Reactor-Wax Analyses

In order to obtain the carbon number distribution beyond C₅₅, we investigated the application of Field Ionization Mass Spectrometry (FIMS) for F-T reactor-wax analysis.

Wax samples from Runs CT-256-3, -4, and -5 were analyzed. The analysis was carried out by an outside laboratory (SRI International, Menlo Park, CA). For each sample two spectrums covering two molecular weight ranges were obtained. The wide range spectrum covers a molecular weight-range of 100-2000. The two FIMS spectrums for reactor-waxes from Run CT-256-3, -4, and -5 are shown in Figures VI-4, -5, and -6, respectively. In these figures the corrected intensity is plotted as a function of molecular weight. Because of the wide range of molecular weights, a unit-mass resolution cannot be obtained for these spectrums. The corrected intensity is proportional to the molar content. In all these cases the response factors for different hydrocarbon types (like olefins, paraffins, oxygenates, etc.) are unknown. The area under the curve gives the total mass. To compare these results to the GC results, we have estimated the C₅₅⁺ content from these spectrums. Table VI-3 summarizes the results and shows the similar C₅₅⁺

Table VI-2
 Composition of a
Fischer-Tropsch Reactor-Wax
 (Run CT-256-4)

<u>TBP Fraction (°C)</u>	<u>Distillation</u>	<u>New GC Analysis</u>
343-	1.1	1.9
343-399	2.5	3.9
399-454	7.0	6.2
454-461	6.3	1.9
461+	<u>83.1</u>	<u>86.1</u>
Total	100.0	100.0

Unit: Wt %

Figure VI-2

**SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE
FISCHER-TROPSCH PRODUCTS**

FRAC. CLASS-4, 26.3 G/G
REACTOR-WAX YIELD - 46 WTM%

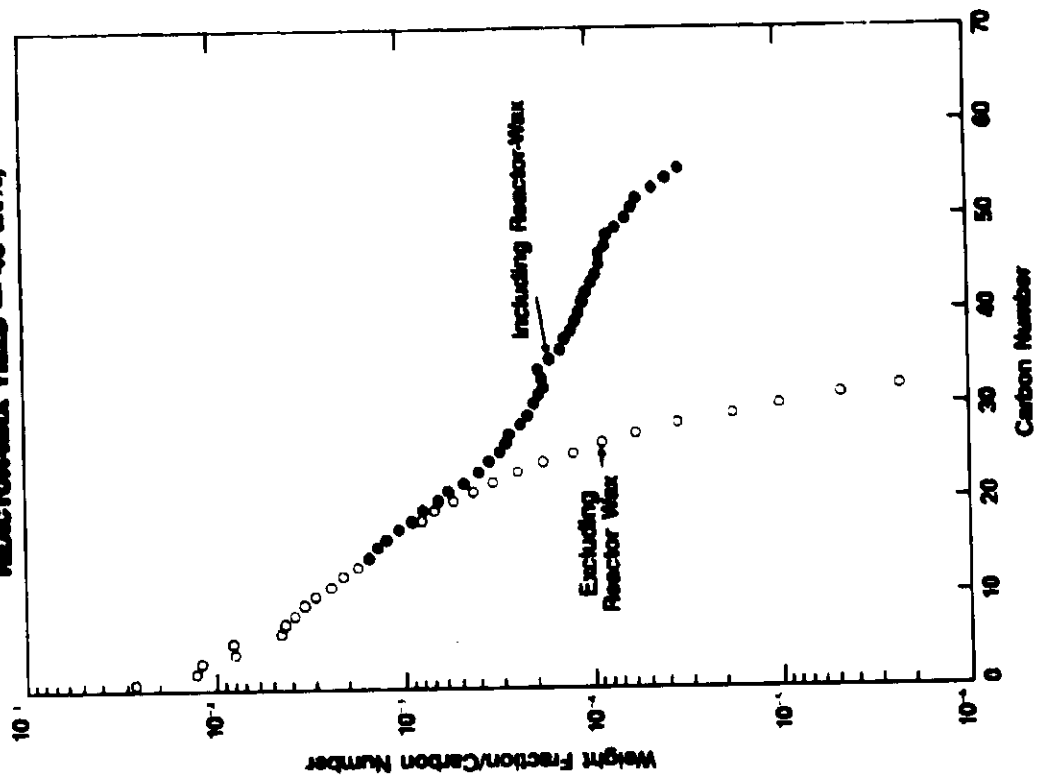


Figure VI-3

**SCHULZ-FLORY DISTRIBUTION FOR FIRST-STAGE
FISCHER-TROPSCH PRODUCTS**
RUN CT-250-6, 8.6 DCS
REACTOR-MAX YIELD - 77 Wt%

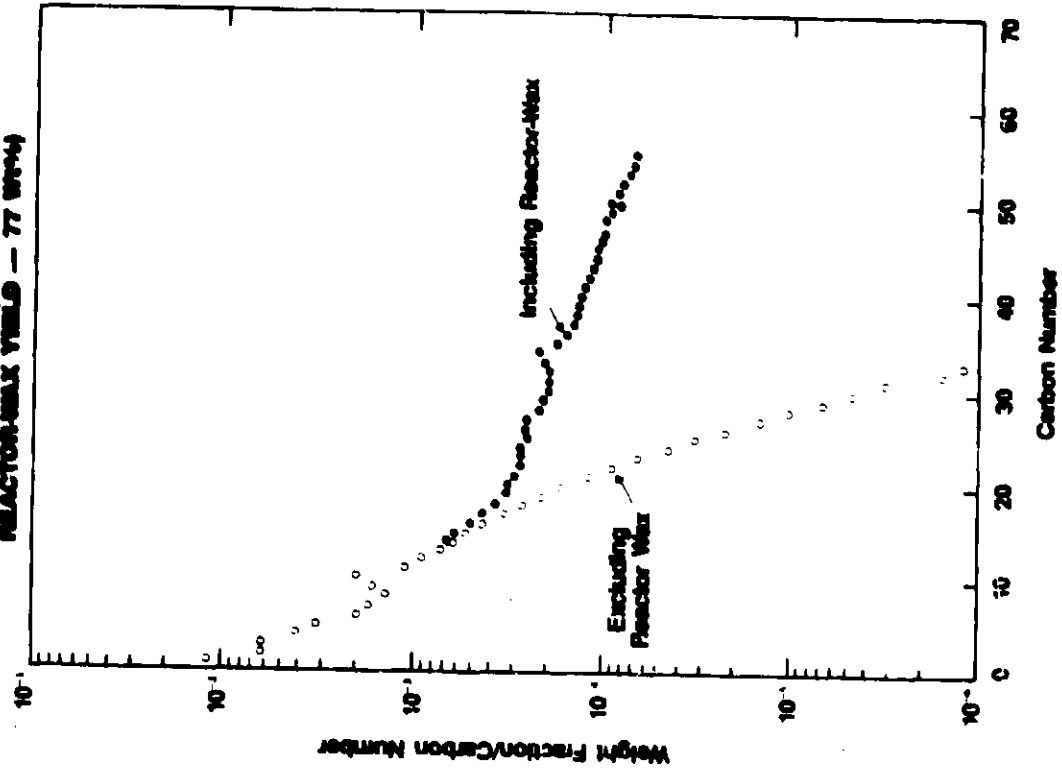


Figure VI-4
FIMS SPECTRUM OF RUN CT-256-3 REACTOR-WAX
(WIDE RANGE)

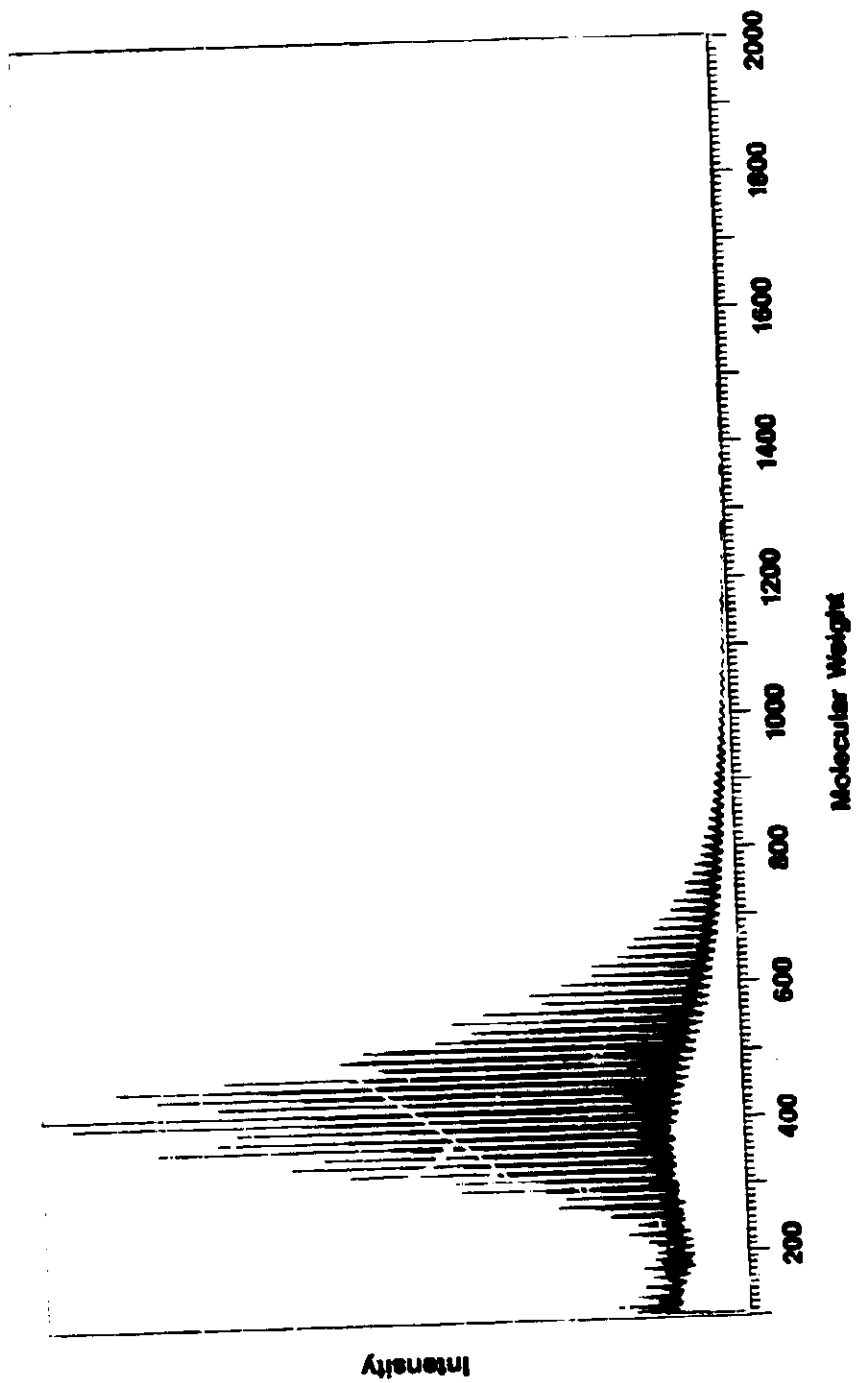


Figure VI-5
FIMS SPECTRUM OF RUN CT-256-4 REACTOR-WAX
(WIDE RANGE)

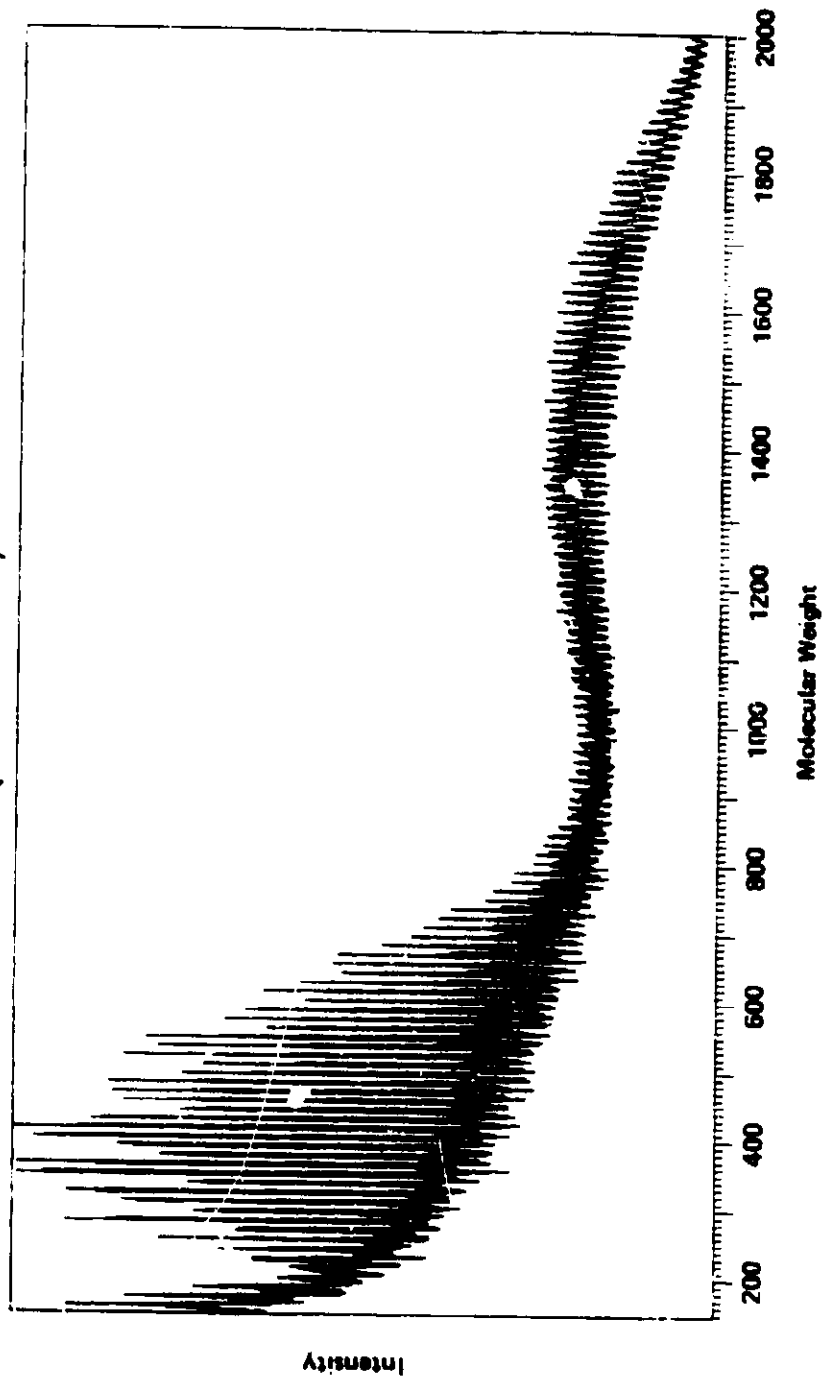


Figure VI-6
FIMS SPECTRUM OF RUN CT-256-5 REACTOR-WAX
(WIDE RANGE)

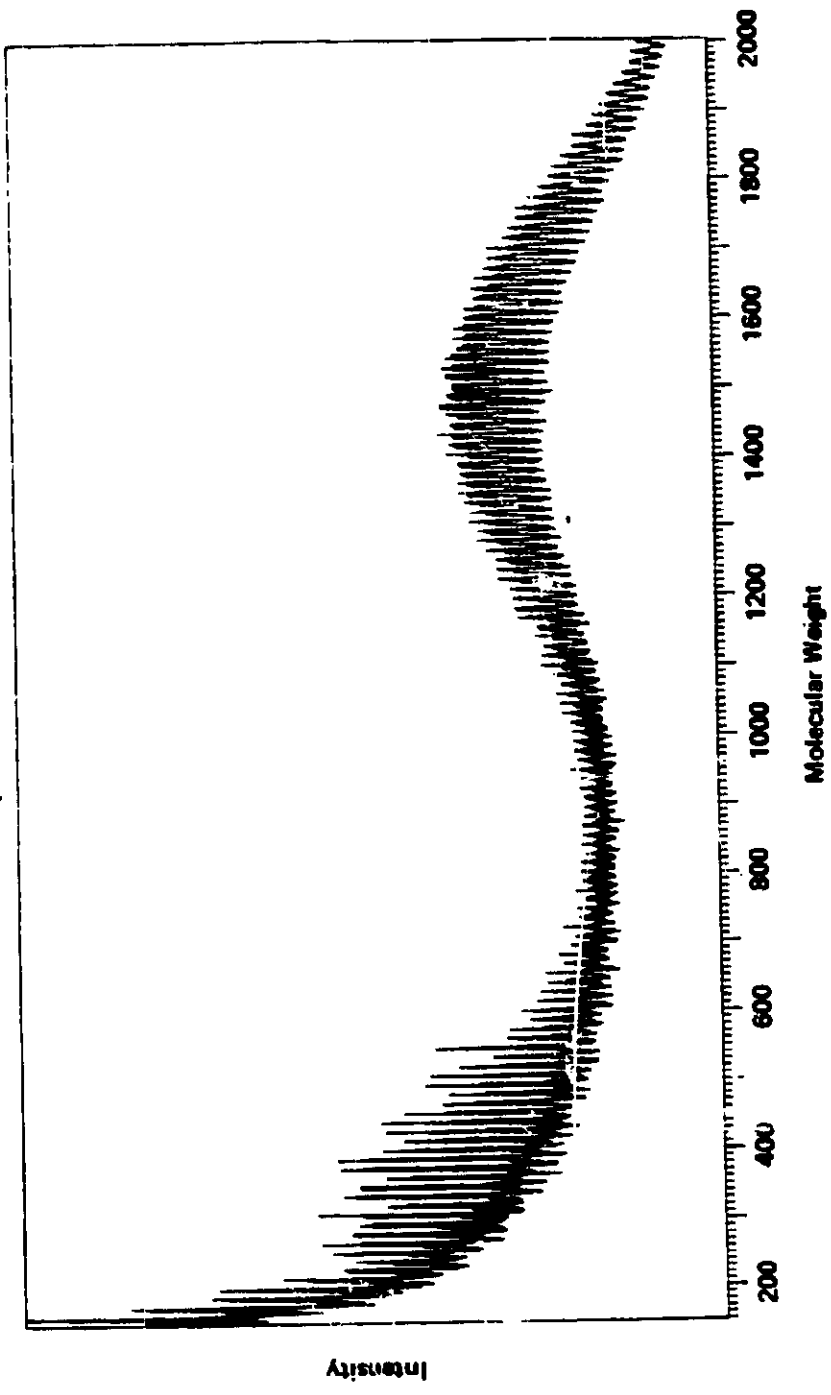


Table VI-3
FIMS Analysis of
Reactor-Waxes

	<u>Run</u> <u>CT-256-3</u>	<u>Run</u> <u>CT-256-4</u>	<u>Run</u> <u>CT-256-5</u>
C ₅₅ ⁺ Content, wt %	6	64	72
C ₅₅ ⁺ Content Based on GC, wt %	6	65	75
Molar Avg. MW (Avg. Carbon No.)	460 (33)	814 (58)	976 (70)
Weight Avg. MW (Avg. Carbon No.)	598 (42)	1,135 (81)	1,291 (92)

contents for all three reactor-waxes by both methods. Table VI-3 also gives number average and weight average molecular weights for these reactor-waxes. The increasing molecular weight for these waxes (from Run CT-256-3 to Run -5) is consistent with the increasing viscosity observed.

Since the wide-range spectrum did not resolve intensity peaks for each mass, no digitized data other than the spectrum shown here was provided by SRI International. In order to obtain a carbon-number distribution plot (or molecular weight distribution), it is necessary to obtain the area under each peak. However, it is very difficult to do this for peaks below ~800 molecular weight, since they are very crowded. Hence, only the peaks beyond molecular weight 800 were considered. The carbon-number distribution below molecular weight 800 was obtained from another, higher resolution, spectrum.

Figure VI-7 shows a typical high-resolution spectrum obtained over a molecular weight range of 100 to 800. In this range a unit-mass resolution is achieved, but the span of the molecular weight is limited to 700 up to 1,300. The y-axis for this high-resolution spectrum is the percent of total moles seen by the spectrometer (i.e., between 100 to 800 molecular weight). Once again, as in the case of wide-range spectrum no correction has been made for response factor of different hydrocarbon types, for effect of different molecular weights, and also for C^{13} isotope contribution. Since the percentage of the molecules that contain C^{13} isotope increases with increasing molecular weight, it becomes increasingly important to take this into consideration for the higher molecular weight hydrocarbons.

Since no response factors of hydrocarbon types and of molecular weights over this molecular weight range are available, we have used those obtained up to C_{20} (molecular weight <250). The high-resolution spectrum thus gave a carbon number distribution over the molecular weight range of 100-800. By combining the distribution obtained from the low-resolution (wide-range) data for the molecular weight range >800, a complete carbon-number distribution was obtained as given in Figure VI-8. As seen in the figure, a bimodal carbon-number distribution is revealed for the Run CT-256-5 wax. The second hump at carbon-number of about 105 has been observed for the first time for F-T waxes. As evident from the wide-range spectrums (Figures VI-4 to -6), the Run CT-256-3 reactor-wax did not exhibit a second hump. The carbon number distribution below C_{55} agrees well with that obtained from the modified GC method. The presence of a second hump in the carbon-number distribution cannot be explained at this time.

Figure VI-7
FIMS SPECTRUM OF RUN CT-256-5 REACTOR-WAX
(HIGH RESOLUTION)

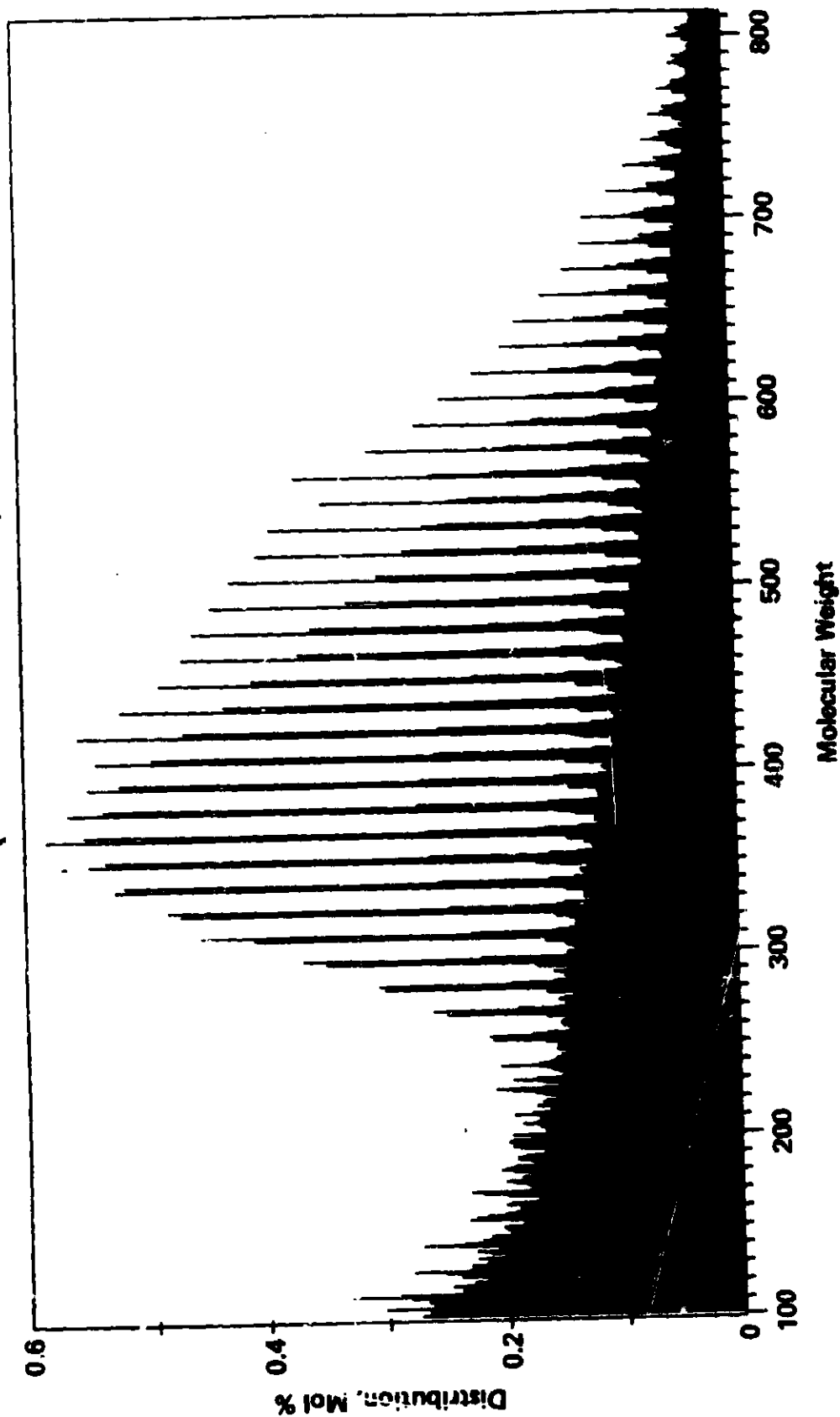
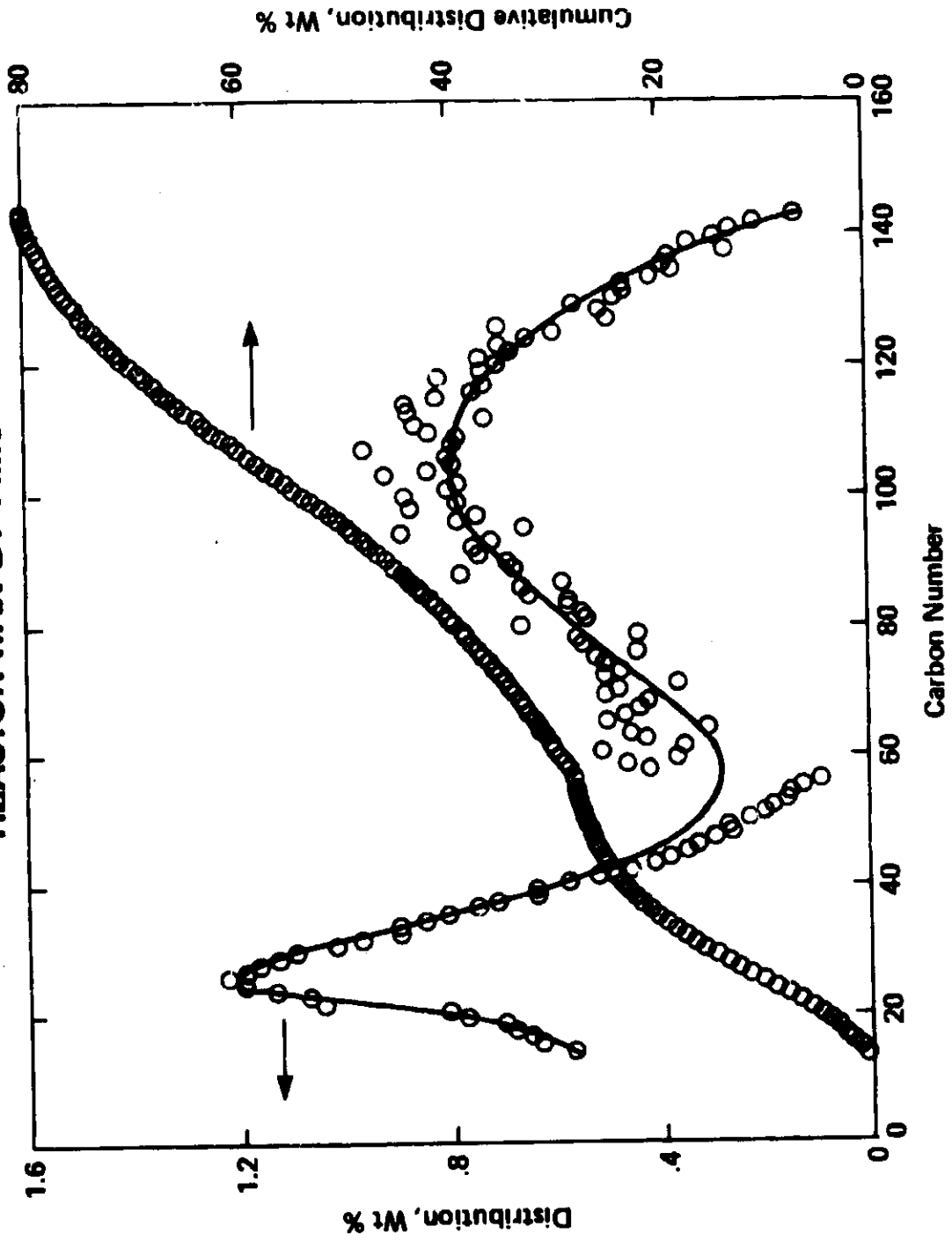


Figure VI-8
CARBON-NUMBER DISTRIBUTION OF RUN CT-256-5
REACTOR-WAX BY FIMS



We also analyzed CT-256-7 reactor-wax using FIMS. The sample was obtained from a homogenized blend of the reactor-waxes produced throughout the run. This is the same blend from which the DOE was supplied with a 22 kg sample. The raw FIMS spectrum of the wax is shown in Figure VI-9. Table VI-4 compares the C_{55}^+ content to that for Run CT-256-4 reactor-wax which was produced under similar operating conditions and using the same catalyst. The similarity between the two waxes are clearly evident from the table.

Since there is no prior experience with the FIMS analysis of heavy F-T waxes, the extent of fragmentation of the heavy molecules during the analysis is unavailable. We therefore re-analyzed CT-256-4 and -5 reactor-waxes in such a way as to shed more light on this phenomenon.

The spectrums from earlier analyses of these waxes are shown in Figures VI-5 and VI-6. As explained earlier the C_{55}^+ content of these waxes were estimated using the areas under the peaks of molecular weight larger than 772. We also assumed that all the peaks below 200 MW were the result of fragmentation of molecules heavier than 772 (i.e., C_{55}^+). Hence, these peak areas were added to the C_{55}^+ content. This amount of material below 200 MW of CT-256-4 and -5 reactor-waxes were 7.2 and 7 wt % of the total sample, respectively.

The new analyses were carried out in the following manner. While the temperature of the sample was raised from -17 to 451°C, the ionic intensity were counted only in the 50 to 800 MW range. It was found that evolution of lower masses below 200 and particularly the 56, 57, and 71 MW ions continuously increased during the temperature scan. The intensity increase of these masses increased substantially above 270°C, at which only molecules heavier than ~800 are expected to evolve. The low masses evolving at these higher temperatures can be interpreted to be the result of fragmentation. It was also noticed that during this fragmentation at high temperatures, the intensity increase of the peaks between 200-770 MW was very minimum; most of the intensity increase was in 50-200 range. The increase of intensity between 200-770 MW after ~200°C was estimated to be less than 5%. This observation implies that fragmentation of the large molecules occurs at their tails and not in the middle of the chains, thus producing very small (C_3 - C_4) chains. The amount of material below 200 MW estimated from these analyses were very close to the previous estimates for both reactor-waxes (i.e., 7.2 and 7 wt %). Hence, no corrections to the previous analyses are required.

It is also possible to qualitatively explain the presence of a second hump at ~1,500 MW, assuming that the fragmentation of molecules heavier than 1,700-1,800 MW is

Figure VI-9
FIMS SPECTRUM OF RUN CT-256-7 REACTOR-WAX
(WIDE RANGE)

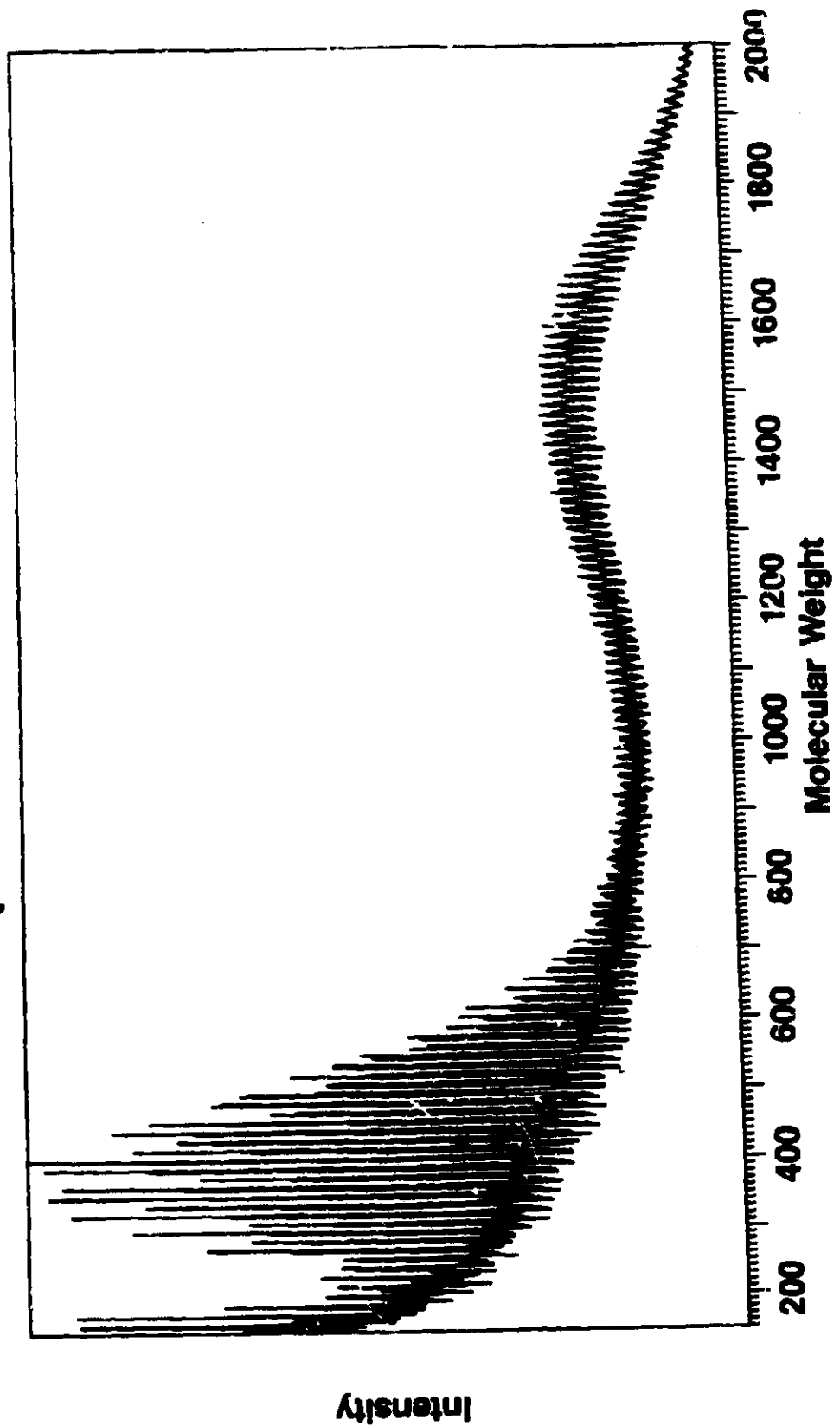


Table VI-4
 Results of FIMS
Analysis of Reactor-Waxes

	<u>Reactor-Waxes*</u>	
	<u>CT-256-7</u>	<u>CT-256-4</u>
C ₅₅ ⁺ Content, wt %	60.3	65.0
Molar Avg. MW	857	814
Weight Avg. MW	1,189	1,135

*Both Runs CT-256-4 and -7 used the same Catalyst I-B and were run in low methane + ethane mode under similar operating conditions.