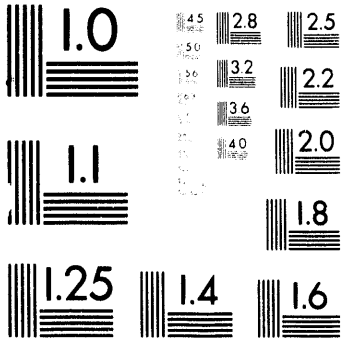
1.0
2.8
2.5
3.2
2.2
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

1 of 1

DOE/PC/90055-T9

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

CONTRACT DE-AC22-90PC90055

Technical Progress Report No. 8
7/1/92 - 9/30/92

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PATENT CLEARED BY CHICAGO
OPC ON November 15, 1993

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

Contract DE-AC22-90PC90055

Technical Progress Report No. 8
(7/1/92-9/30/92)

by
Robert R. Frame and Hemant B. Gala

UOP
25 E. Algonquin Road
Des Plaines, Illinois

Contract Objective

The objectives of this contract are to develop a technology for the production of active and stable iron (Fe) Fischer-Tropsch catalysts for use in slurry-phase synthesis reactors and to develop a scaleup procedure for large-scale synthesis of such catalysts for process development and long-term testing in slurry bubble-column reactors. With a feed containing hydrogen (H_2) and carbon monoxide (CO) in the molar ratio of 0.5 to 1.0 to the slurry bubble-column reactor, the catalyst performance target is 88% $CO+H_2$ conversion at a minimum space velocity of 2.4 NL/hr/gFe. The desired sum of methane and ethane selectivities is no more than 4%, and the conversion loss per week is not to exceed 1%.

Contract Tasks

Task 1.0: Catalyst development
- 1.1: Technology assessment
- 1.2: Precipitated catalyst preparation method development
- 1.3: Novel catalyst preparation methods investigation
- 1.4: Catalyst pretreatment
- 1.5: Catalyst characterization

Task 2.0: Catalyst testing
Task 3.0: Catalyst aging studies
Task 4.0: Preliminary design and cost estimate of a catalyst synthesis facility

Scope of Work Reported

The work reported in this technical progress report covers a new technique developed to add potassium (K) to the iron-copper oxide catalyst and testing of two catalysts prepared by using this technique.

The use of an alkali promoter like K to suppress the formation of methane is widely practiced. The objective of developing a novel K-addition technique was to simplify the method of catalyst preparation by reducing the steps involved and to have an external control over the selectivity of the iron catalyst to methane formation.

In the new method a potassium salt of a long-chain carboxylic acid (e.g. potassium laurate) is added to a mixture of the iron-copper oxide composition and an oil (typically a C_{30} oil) in the slurry autoclave. The resulting mixture can be activated by a standard method to produce a slurry-phase Fischer-Tropsch catalyst. In performance such a catalyst exhibits comparable H_2 and CO conversions and product selectivities as a catalyst prepared by the aqueous impregnation of potassium carbonate followed by calcination.

Experimental Procedures

For tests reported in this technical progress report, UOP's standard procedure for activation and testing was used. The slurry autoclave reactor used for these runs is contained in a hot box which is maintained at 130°C. The liquid and gaseous products are separately withdrawn but taken to the same traps. There are three traps in series the first is in the hot box, the second and third are outside of the hot box and maintained at ice and dry ice/acetone temperatures, respectively. A small slip-stream of the product before the ice trap is taken to a gas chromatograph (GC), GC-1, for an on-line boiling point analysis. A second slip-stream (after the ice trap) is taken to a second GC, GC-2, for an analysis of the light gases (C_1 to C_4). Periodically the total product (CO_2-free basis) is analyzed by a mixture of off- and on-line methods as follows: the gases by on-line GC, the contents of the hot box trap (wax) by off-line gel phase chromatography (GPC), and the contents of two cold traps by off-line GC.

Run Summary

Run 42

Ten grams of potassium laurate were used with seventy-three grams of iron-copper oxide (Table 1). The iron : potassium weight ratio was 100 : 3.2. Based on previous work with catalysts prepared by aqueous impregnation of potassium carbonate onto iron-copper oxide followed by calcination, this ratio is higher than needed for optimum conversion and low methane + ethane selectivity (Report No. 4, current contract). However, at the outset of this work it was not known whether there would be a correspondence between the two potassium addition methods, therefore, two levels of potassium were investigated: the level used in this run and the lower level used in Run 43.

The conditions for initial part of this run were the same as those used in previous runs with catalysts prepared by the potassium impregnation method. After about fifty hours-on-stream the conversions appeared to be lined-out, for instance, the CO conversion was 60%. This conversion is about what one would expect based on previous work in this laboratory for similar K-level catalysts resulting from potassium carbonate impregnation.

Plots of conversions and light product selectivities (GC-2 data) vs. hours-on-stream are in the Appendix as Figures A-1 to A-6. The methane selectivity was quite low as expected due both to the relatively low conversion and the high level of potassium. Previous work in these and other laboratories has shown that methane selectivity decreases as the potassium level increases or the conversion decreases. Selectivities to the other light products were also low, this again was expected based on previous work. A plot of olefin/paraffin ratio vs. carbon number is in Figure A-7. These data are from GC-1 and illustrate the known fact that the Fischer-Tropsch product becomes less olefinic as the carbon number increases.

The liquid level in the autoclave is always allowed to build to a target from the initial low level, but thereafter the level is maintained by periodic liquid withdrawals. A constant level at about seven inches from the bottom of the autoclave is desired. The liquid level can be determined by measurements of the internal reactor temperatures vs. distance from bottom of the reactor. Figure A-8 is a plot of the liquid level vs time and shows that the liquid level was maintained at seven inches except for a brief period around sixty-five hours-on-stream.

At 145 hours-on-stream the space velocity was halved, as a result the conversions increased to levels very nearly the same as in the earlier Run 37 which utilized the most active of this contract's potassium carbonate impregnated catalysts, but at the initial, higher space velocity. Conversions and selectivities from Runs 37 and 42 are summarized in Table 1. In Run 42 the increased conversion induced by the lower space velocity also resulted in an increase in the methane selectivity as expected. However, the methane selectivity at 70% CO conversion was significantly lower than that of the Run 37 catalyst at a similar (76%) CO conversion. The other light hydrocarbon selectivities did not seem to be affected by the space velocity change. However, there were increases in the light alcohol selectivities after the space velocity change.

A complete analysis of the total product was made for three twenty-four hr periods of this run. These three periods covered the following times-on-stream: 25-48 hrs, 97-120 hrs and 145-168 hrs. The product composition was determined by on-line GC analysis of the product gas (C_1-C_4), off-line GC analyses of the contents of the wet and dry ice traps and off-line GPC analysis of the contents of the hot box trap. The traps do not do an adequate job of collecting the C_5's and C_6's, therefore, these concentrations were no doubt higher than found. A sample wax GPC analysis is shown in Figure A-9. Wax and GC analyses are summarized in three Lotus spreadsheets, one each for the three periods, Figures A-10 to A-12. From these analyses the weight percent of the total product at each carbon number on a CO_2-free basis (sum from all traps) as well as the natural logarithm of the ratio of wt% at a carbon no. to the carbon no. was calculated. These data are summarized in a wt% of total product vs carbon number plot (Figure A-13), and Schulz-Flory plots and attached as Figures A-14 to A-19. Figure A-13 illustrates

that the values for C_5 and C_6 are low, this is because the traps do not do an adequate job of trapping these products. The Schulz-Flory plots include full range and partial (C_1-C_{20}) Schulz-Flory plots all of which are parabolic (so-called "double alpha") plots. Such double alpha plots have been observed before. A modified non-linear least squares method was used with the C_1-C_{20} data to calculate values for alpha-1 and alpha-2 as well as XI which is the carbon number "breakpoint": the carbon number at which two straight lines defined by the "linear" portions of the parabolic Schulz-Flory plot meet. The summary plots also include Figure A-20 which reports the weight percent of the total product in each of the historic fuel distillation ranges: gas (C_1-C_4), gasoline (C_5-C_{12}), diesel (C_{13}-C_{19}) and heavy (C_{20+}). The increase in light ends selectivity and the compensating decrease in wax yield due to the space velocity change are clearly visible in this plot.

Run 43

Potassium laurate was used again but in a lesser amount to provide a potassium level equal to that present in Run 37. Run 37 was the best previous run from the standpoint of low methane + ethane selectivity and high conversion. Although the iron-copper oxides used in Runs 37 and 42 were from different batches it was hoped that with similar potassium levels the catalyst performance during the two runs would be similar.

The initial operating conditions for this run were the same as Run 37; these conditions were maintained until an apparent line-out in conversions and selectivities was achieved. Plots of conversions and light product selectivities vs. hours-on-stream are attached as Figures A-21 to A-26. Line-out conversions and selectivities from Runs 37, 42 and 43 are compared in Table 1. The CO conversion and methane/ethane selectivities for Run 43 were close to those of Run 37. It appears, therefore, that the simple addition of potassium laurate at the beginning of the run can replace the more time-consuming potassium carbonate impregnation with no ill effect to the catalyst.

During the latter part of this run space velocity and temperature changes were made to determine product selectivities at different conversion levels. The initial conditions were re-established at the end of the run to confirm that the catalyst had not changed in performance during operating condition excursions.

Analysis of the total liquid product was performed for three twenty-four hr periods (Period 4, 72-96 hrs; Period 9, 192-216 hrs, and Period 15, 336-360 hrs). The Lotus spreadsheets which summarize these analyses are attached as Figures A-27 to A-29. The Schulz-Flory plots and the bar plot of gas, gasoline, etc. which were prepared from the spreadsheet data are attached as Figures A-30 to A-36.

Figure A-37 is a plot of autoclave liquid level vs. hours-on-stream. Except for a few times the liquid level was within one-half inch of the seven inch level target.

The data from the condition changes are summarized in Figures A-38 to A-48. Two types of plots are represented in these Figures: selectivity vs. conversion and yield (selectivity times conversion) vs. contact time. The latter plots are helpful in determining which products are primary and which are secondary.

Figure A-38 is a selectivity vs. conversion plot for methane. The methane selectivity is greater at higher conversion presumably because the H_2 : CO ratio increases as the conversion increases. Figure A-39 is a yield vs. contact time plot for methane, which shows methane formation at very short contact times. Methane, therefore, appears to be a primary product from the reaction of synthesis gas. There is no downward bend to the plot at long contact times which indicates that methane isn't converted into secondary products.

Figures A-40 to A-42 are yield vs. contact time plots for ethylene, ethane and ethanol. From these it appears that ethylene is a primary product which appears to be consumed at high contact times whereas ethane is a secondary product. The easiest guess as to the mechanism is that ethane results from hydrogenation of ethylene. Ethanol appears to be a primary product. (Yields for all the alcohols at the highest contact time are questionable because of the unstable alcohol selectivities at this condition-see alcohol selectivity vs. hours-on-stream plots in the Appendix.) Figures A-43 to A-48 are yield vs. contact time plots for C_3 and C_4 hydrocarbons and alcohols. Unlike ethane both propane and butane appear to be formed as primary reaction products. There is indication from the data at 255°C that propanol and butanol are formed as secondary reaction products.

Conclusions

A new, shorter, method for applying potassium to the iron-based Fischer-Tropsch catalyst has been developed. This method uses a potassium salt of a long-chain carboxylic acid which probably has enough solubility in the slurry oil present at start-up so that the potassium can be effectively transferred to the iron oxide catalyst. The resulting catalyst has nearly the same performance properties as one prepared by impregnation of potassium carbonate followed by calcination.

Plans for the Next Quarter

Additional experiments are contemplated with potassium laurate-derived catalysts. One specific approach will be to dissolve the potassium laurate in an organic solvent and add it to the slurry autoclave during a run. This might make it possible to adjust the conversion and/or selectivity during a run.

TABLE 1
PERFORMANCE SUMMARY: TWO POTASSIUM ADDITION METHODS (LINED-OUT CATALYSTS)

PLT/RUN NO.	701/37	701/42	701/43
K ADD. METHOD	K_2CO_3 IMPREG.	SOLID K LAURATE TO RX AT STARTUP	
CATALYST			
OXIDE PART, g	73	73	73
Fe, WT %	64.2	62.2	62.2
K, WT %	1.3	0.0	0.0
Fe:K, WT	100 : 2.1	—	—
K LAURATE, g		10	6.5
Fe:K, WT (TOTAL)	100 : 2.1	100 : 3.2	100 : 2.1
TEST CONDS.			
TEMP, °C	265	265	265
PRESS, PSIG	290	290	290
FEED RATE, (NL/HR • g Fe)	2.4	1.4	2.4
PERFORM. SUM.			
CONVER., %			
CO	76	70	70
H_2	62	58	60
PRODUCTIVITY (M CO/HR • g AT. Fe)	2.5	1.4	2.3
SELEC., MOLE %			
C_1	3.8	2.5	4.1
C_2	1.0	0.7	1.1
$(C_1 + C_2)$——>	4.8	3.2	5.2
$C_2^=$	3.0	2.5	2.7
CO_2	47	45	47

1. FROM K_2O_3 IMPREGNATION

FIGURE A-1

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

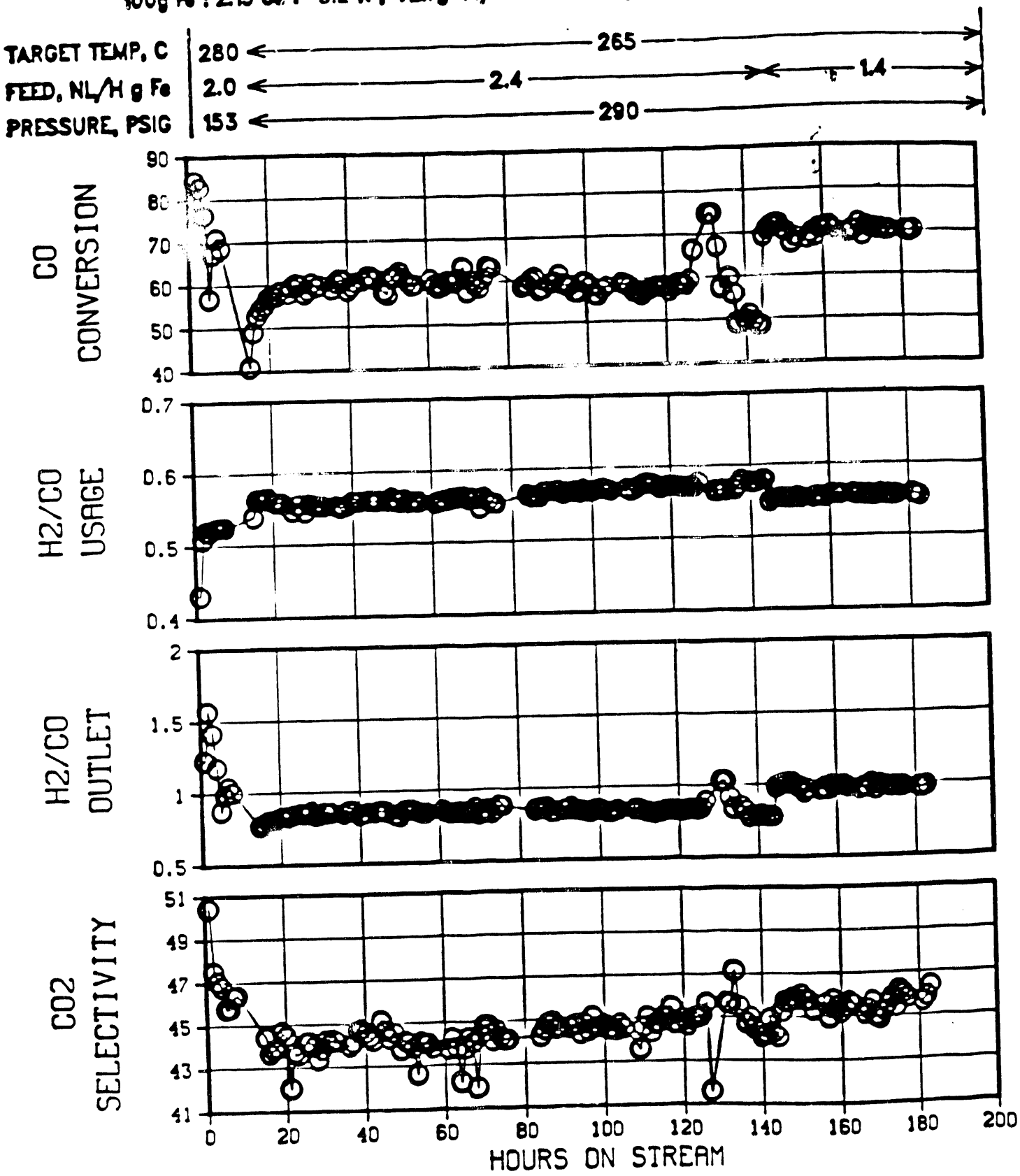


FIGURE A-2

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

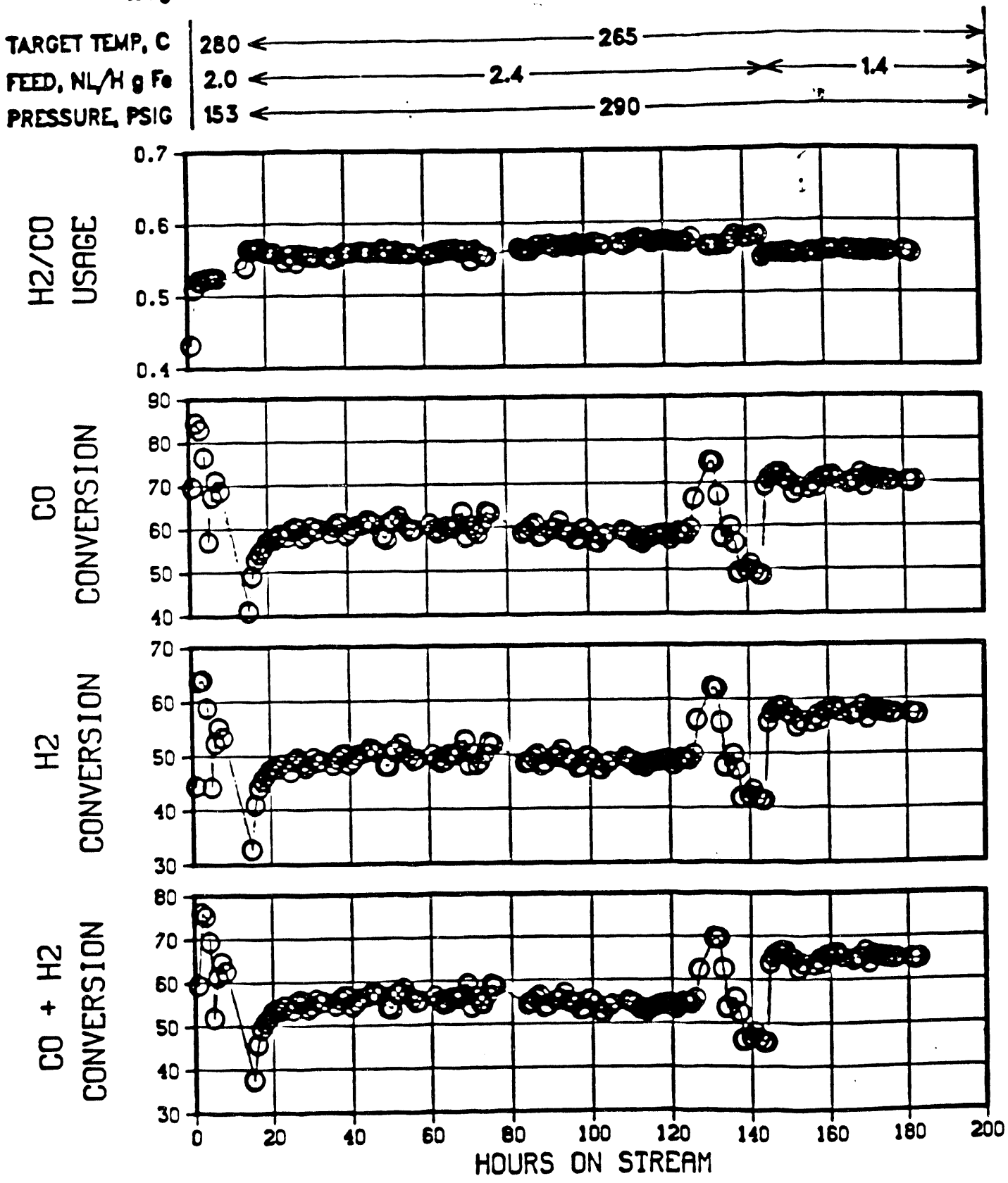


FIGURE A-3

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

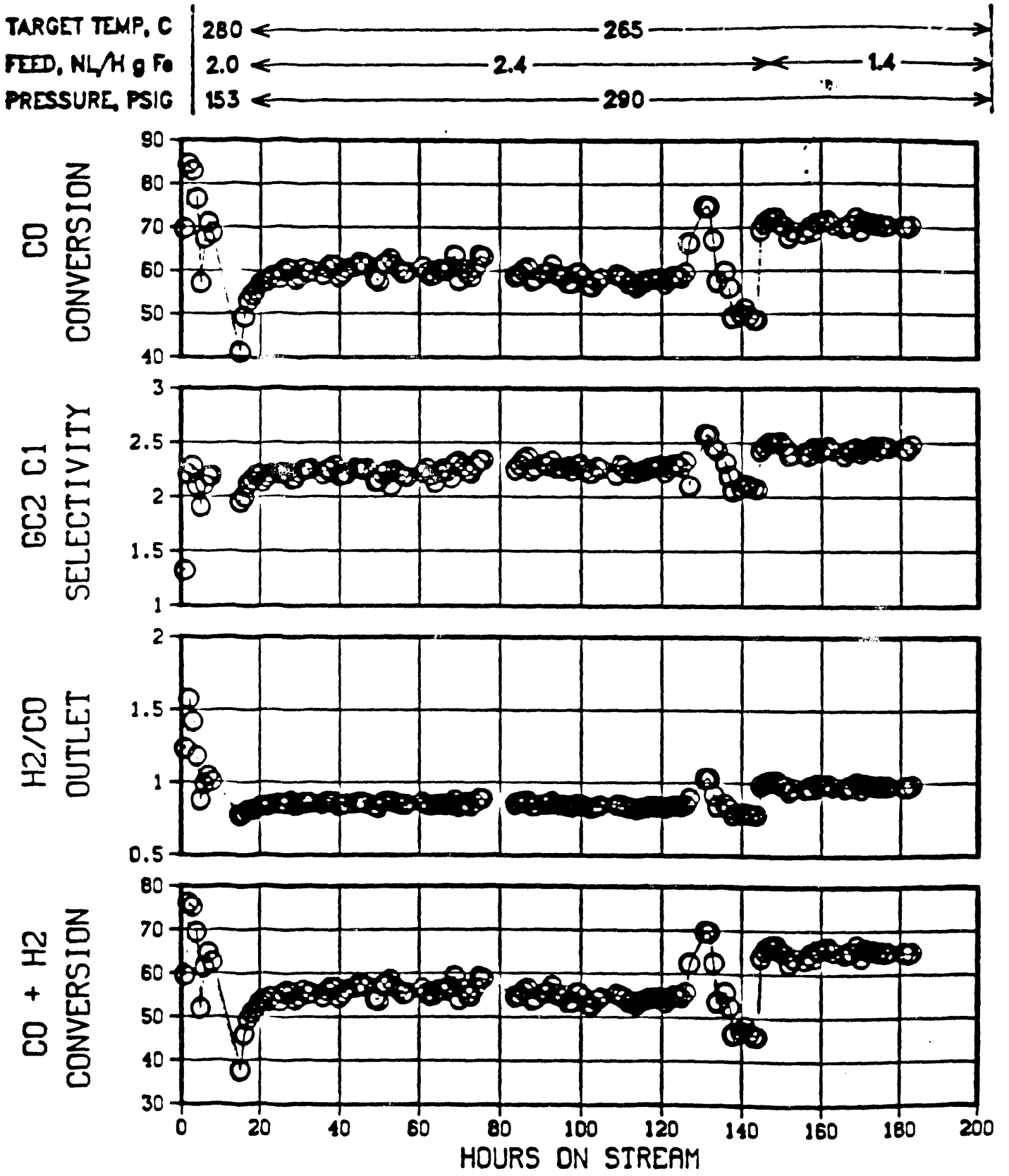


FIGURE A-4

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

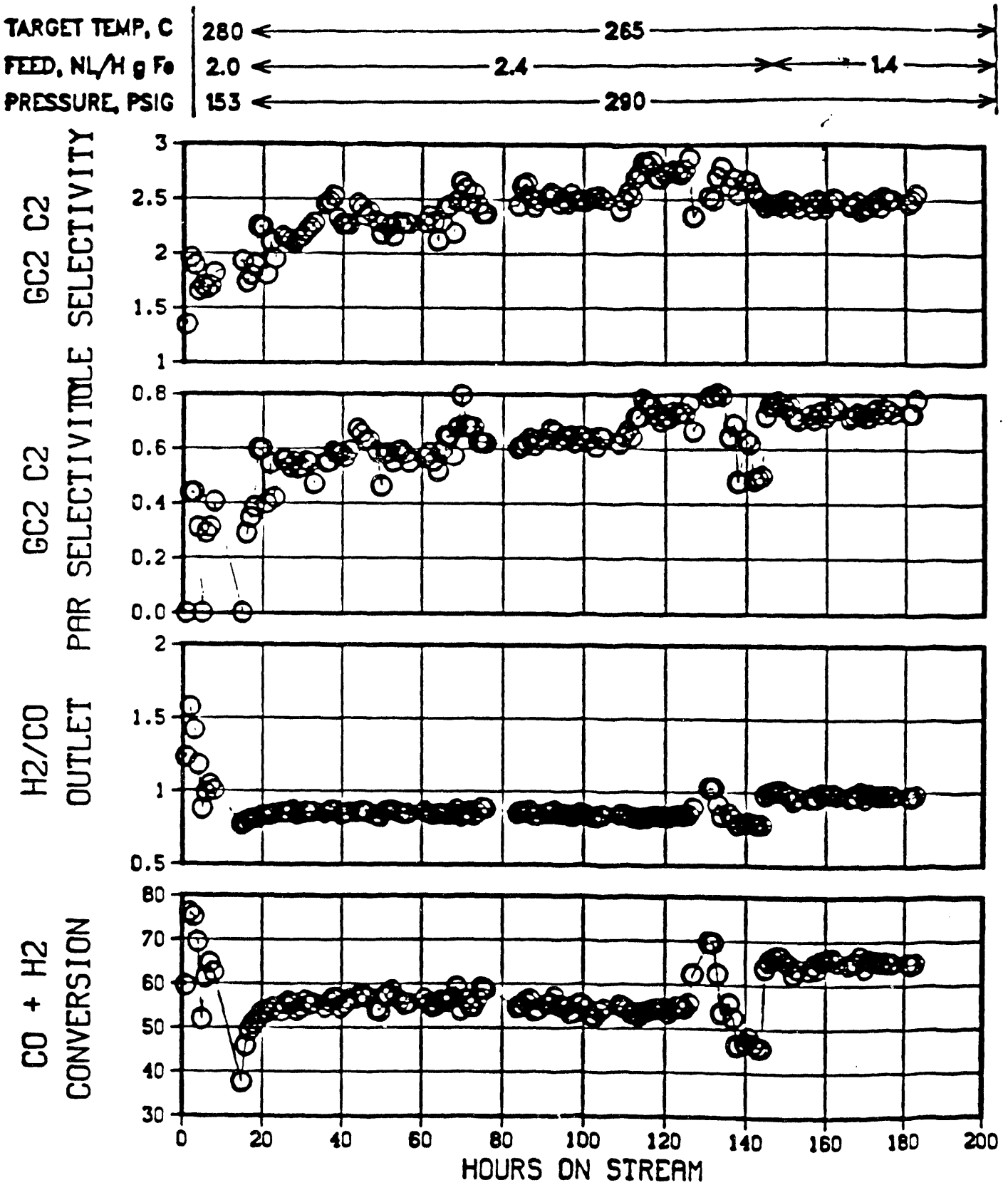


FIGURE A-5

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

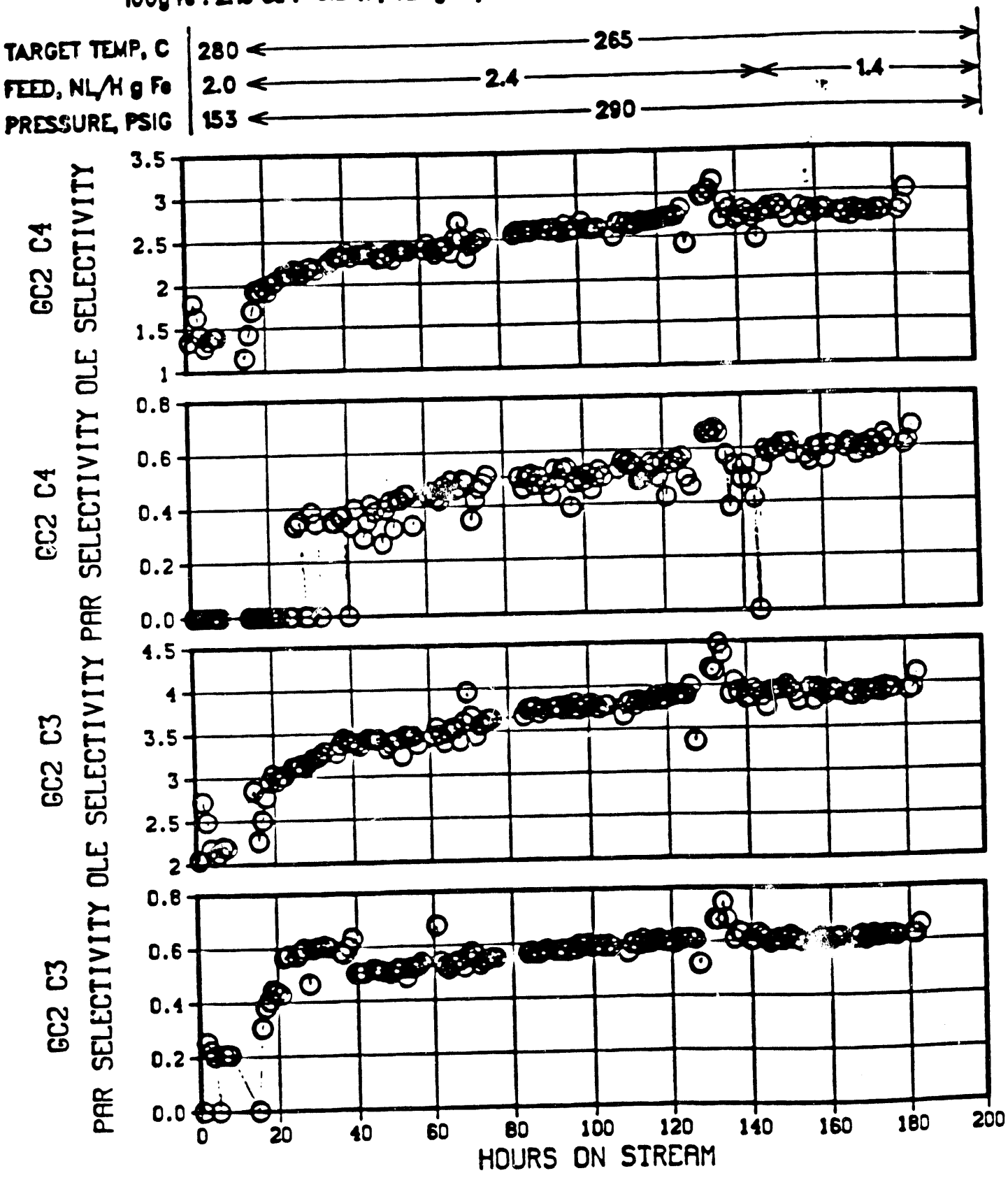


FIGURE A-6

POTTASIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 42 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 3.2 K ; 72.7g Fe/Cu Oxide+10g K Salt in 290 g C_{30} oil

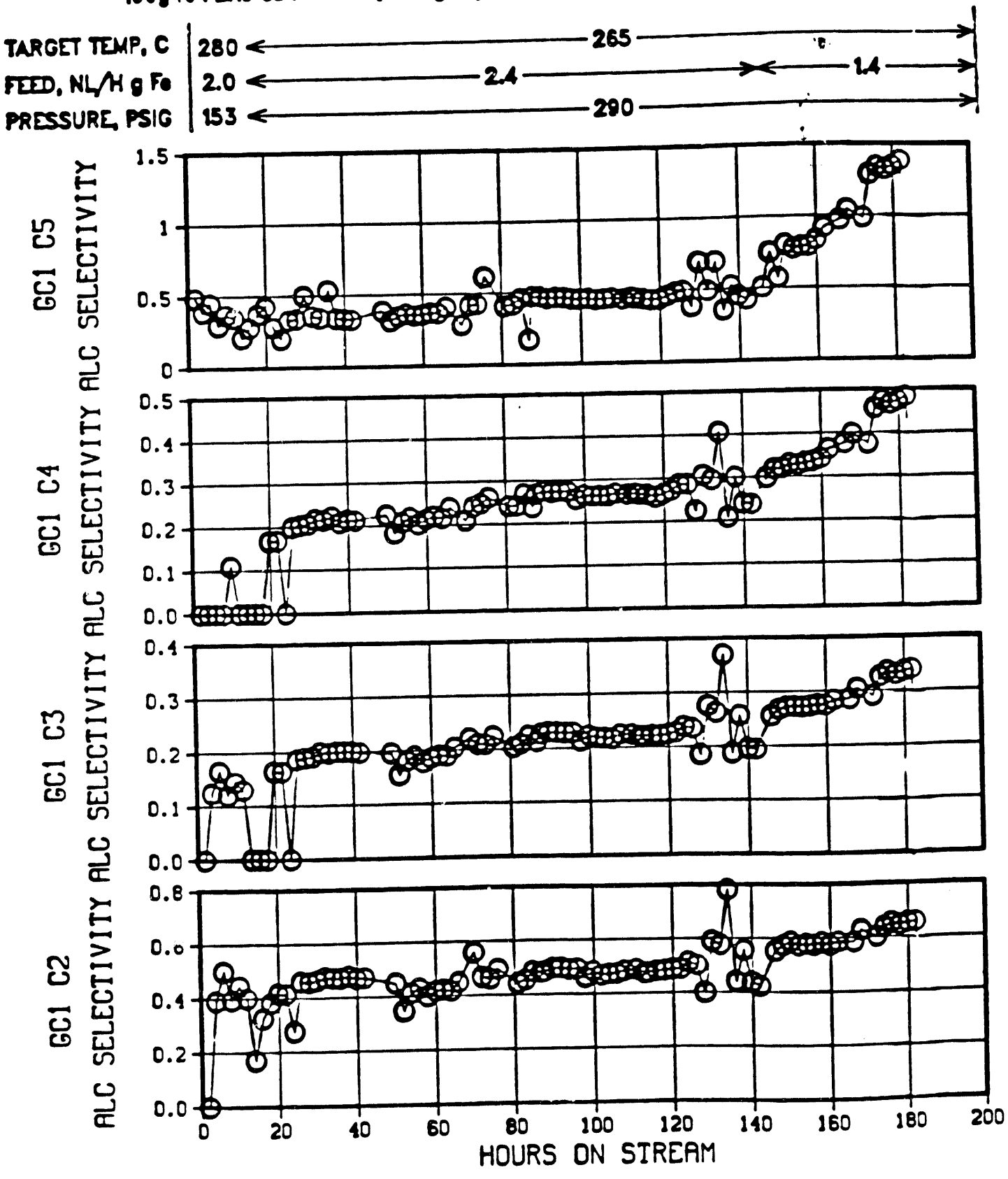


FIGURE A-7

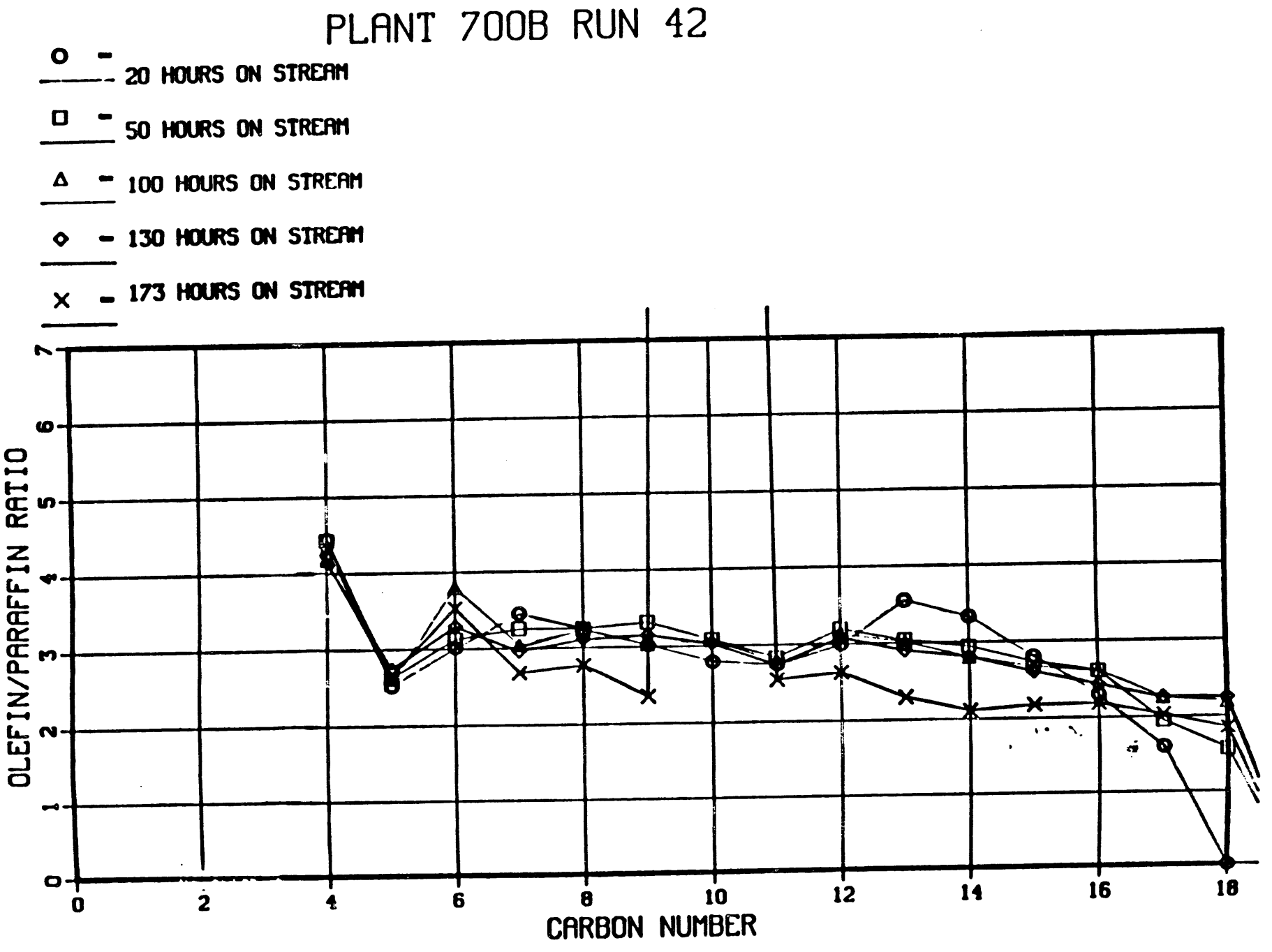
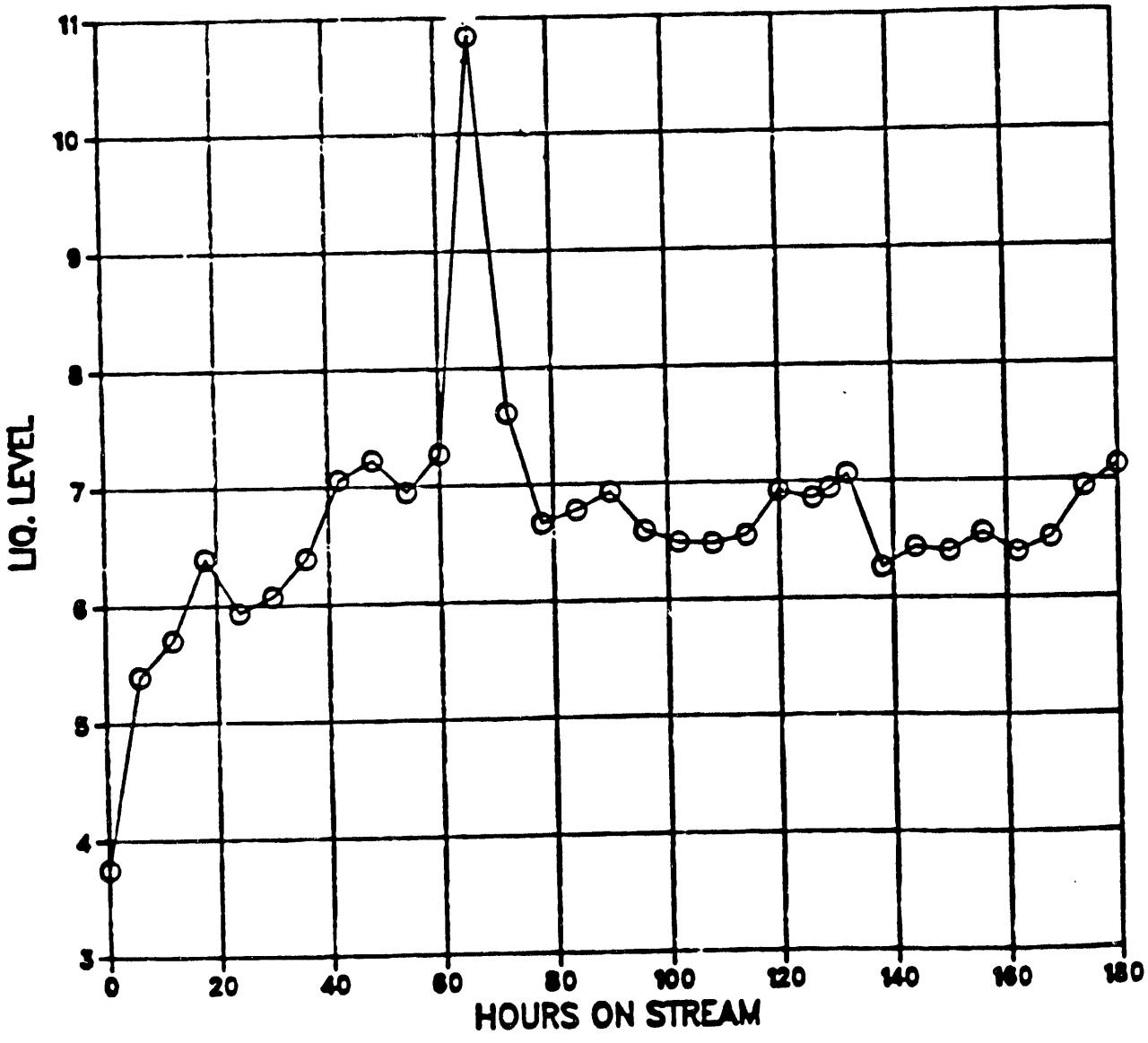

PLANT 700B RUN 42
O - 20 HOURS ON STREAM
□ - 50 HOURS ON STREAM
Δ - 100 HOURS ON STREAM
◇ - 130 HOURS ON STREAM
× - 173 HOURS ON STREAM
OLEFIN/PARAFFIN RATIO
0
1
2
3
4
5
6
7
0
2
4
6
8
10
12
14
16
18
CARBON NUMBER

FIGURE A-8

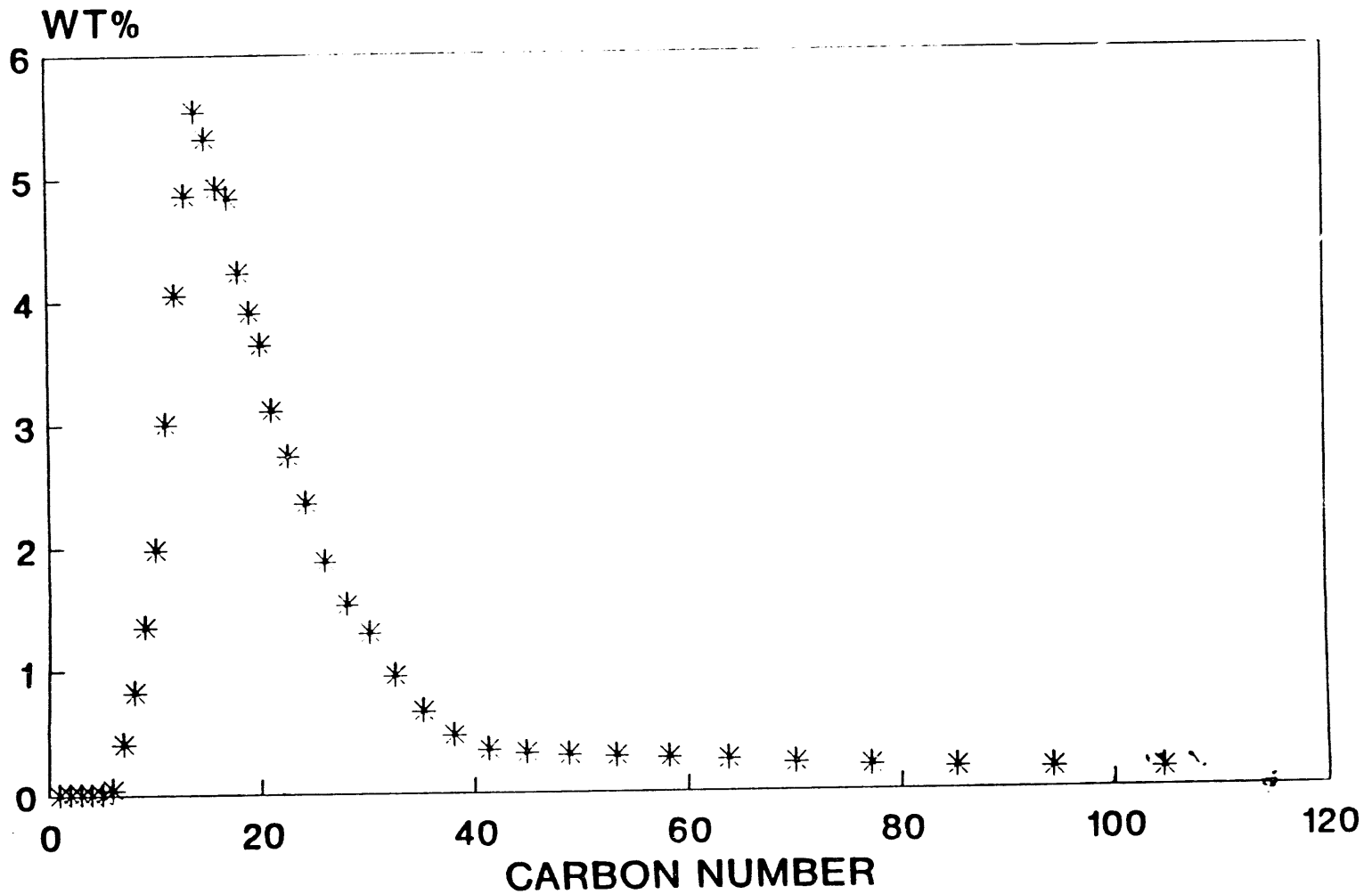
LIQUID LEVEL Vs. HOURS ON STREAM
PLANT 700B RUN 42



(ADAMI.FT)SHEILA.DAT

FIGURE A-9

CORRECTED WAX PRODUCT DISTRIBUTION
PLANT 700B, RUN 42, PERIOD 3



LIU\RUN42\P3-WAX2.CHT

FIGURE A-10

PLANT 700F, RUN 42, PERIOD 3 TOTAL PRODUCTS

C5, C6 CORRECTED USING
C5/C1, C6/C1 RATIO BY GC1

C #	MAX wt%	MAX Gram	ICE AQ Gram	ICE HC Gram	CRYO AQ Gram	CYRO HC Gram	GAS Gram	SUM Gram	MTZ	Ln(MTZ/CN)	
Total	100	62.6	0	25	0	3.03	25.67	121.98			
1	0	0.000	0	0	0	0.037	5.56	5.60	4.59	-3.082	
2	0	0.000	0	1.317	0	0.04	6.16	7.52	6.16	-3.480	
3	0	0.000	0	1.581	0	0.241	8.31	10.13	8.31	-3.587	
4	0	0.000	0	2.833	0	0.563	5.64	9.04	7.41	-3.989	GAS
											26.46
5	0	0.000	0	2.668	0	0.777		7.01	5.75	-4.466	
6	0.04	0.025	0	3.228	0	0.746		5.74	4.70	-4.849	
7	0.4	0.250	0	3.458		0.359		4.07	3.33	-5.347	
8	0.82	0.513		3.129		0.111		3.75	3.08	-5.561	
9	1.35	0.845		2.503		0.071		3.42	2.80	-5.772	
10	1.98	1.239		1.779		0.049		3.07	2.51	-5.986	
11	3	1.878		1.153		0.033		3.06	2.51	-6.082	
12	4.05	2.535		0.725		0		3.26	2.67	-6.107	GASOLINE
											27.36
13	4.86	3.042		0.395		0		3.44	2.82	-6.134	
14	5.54	3.468		0.165		0		3.63	2.98	-6.153	
15	5.32	3.330		0		0		3.33	2.73	-6.309	
16	4.92	3.080		0				3.08	2.52	-6.452	
17	4.84	3.030		0				3.03	2.48	-6.529	
18	4.23	2.648						2.65	2.17	-6.720	
19	3.9	2.441						2.44	2.00	-6.856	DIESEL
											17.71
20	3.64	2.279						2.28	1.87	-6.976	
21.05	3.11	1.947						1.95	1.60	-7.185	HEAVY
22.6	2.73	1.709						1.71	1.40	-7.386	28.46
24.25	2.36	1.477						1.48	1.21	-7.602	
26.05	1.88	1.177						1.18	0.96	-7.901	
28.05	1.53	0.958						0.96	0.79	-8.181	
30.2	1.29	0.808						0.81	0.66	-8.425	
32.55	0.95	0.595						0.59	0.49	-8.806	
35.2	0.66	0.413						0.41	0.34	-9.249	
38.1	0.46	0.288						0.29	0.24	-9.689	
41.3	0.34	0.213						0.21	0.17	-10.072	
44.85	0.31	0.194						0.19	0.16	-10.247	
48.8	0.29	0.182						0.18	0.15	-10.398	
53.25	0.28	0.175						0.18	0.14	-10.520	

PRINTED 09-Jun-93 DATE

FIGURE A-10 (CONT)

63.75	0.25	0.157							0.16	0.13	-10.814
70.05	0.22	0.138							0.14	0.11	-11.036
77.15	0.19	0.119							0.12	0.10	-11.279
85.15	0.17	0.106							0.11	0.09	-11.489
94.25	0.16	0.100							0.10	0.08	-11.651
104.55	0.14	0.088							0.09	0.07	-11.888
120	0.07	0.044							0.04	0.04	-12.719
134	0.17	0.106							0.11	0.09	-11.942
146	0.08	0.050							0.05	0.04	-12.782
164	0.06	0.038							0.04	0.03	-13.186
185.5	0.04	0.025							0.03	0.02	-13.714
210	0.03	0.015							0.02	0.02	-14.126
238.5	0.02	0.013							0.01	0.01	-14.659
272.5	0.01	0.006							0.01	0.01	-15.485
312.5	0.01	0.006							0.01	0.01	-15.622
359	0	0.000							0.00	0.01	ERR
SUM	66.97	41.92322	0	24.934	0	3.027	25.67	100.8573	82.18751		

FIGURE A-11

PLANT 700B, RUN 42, PERIOD 6 TOTAL PRODUCTS

C5 CORRECTED USING C5/C1 RATIO BY GC1

C #	WAX wt%	WAX Gram	ICE AQ Gram	ICE HC Gram	CRYO AQ Gram	CYRO HC Gram	GAS Gram	SUM Gram	WT%	Ln(WT%/CN)
Total	100	166	0	28.99	0	13.98	29.66	248.94		
1	0	0.000	0	0	0	0	5.64	5.64	2.27	-3.787
2	0	0.000	0	0.572	0	0.322	7.55	8.44	3.39	-4.077
3	0	0.000	0	1.1	0	0.284	9.6	10.98	4.41	-4.219
4	0	0.000	0	1.84	0	0.568	6.87	9.28	3.73	-4.676
5	0	0.000	0	2.2	0	0.644		9.96	3.96	-4.938
6	0.04	0.066	0	2.74	0	2.76		8.86	3.56	-5.127
7	0.24	0.398	0	3.84		3.48		7.72	3.10	-5.420
8	0.29	0.481		4.33		2.59		7.40	2.97	-5.595
9	0.59	0.979		3.88		1.65		6.51	2.61	-5.841
10	0.94	1.560		2.94		0.985		5.49	2.20	-6.118
11	1.28	2.125		2.08		0.474		4.68	1.88	-6.372
12	1.66	2.756		1.47		0.17		4.40	1.77	-6.522
13	1.86	3.088		0.898		0.057		4.04	1.62	-6.685
14	2.12	3.519		0.49		0		4.01	1.61	-6.768
15	2.11	3.503		0.286		0		3.79	1.52	-6.893
16	2.03	3.370		0.122				3.49	1.40	-7.039
17	2.07	3.436		0.082				3.52	1.41	-7.092
18	1.88	3.121		0.082				3.20	1.29	-7.244
19	1.8	2.988		0.041				3.03	1.22	-7.353
20	1.73	2.872						2.87	1.15	-7.458
21.05	1.52	2.523						2.52	1.01	-7.639
22.6	1.44	2.390						2.39	0.96	-7.764
24.25	1.37	2.274						2.27	0.91	-7.884
26.05	1.24	2.058						2.06	0.83	-8.055
28.05	1.13	1.876						1.88	0.75	-8.222

FIGURE A-11 (CONT)

30.2	1.09	1.809							1.81	0.73	-8.332
32.55	0.99	1.643							1.64	0.66	-8.503
35.2	0.90	1.494							1.49	0.60	-8.677
38.1	0.86	1.428							1.43	0.57	-8.801
41.3	0.80	1.328							1.33	0.53	-8.954
44.85	0.76	1.262							1.26	0.51	-9.088
48.8	0.72	1.195							1.20	0.48	-9.227
53.25	0.68	1.125							1.13	0.45	-9.371
58.2	0.65	1.079							1.08	0.43	-9.505
63.75	0.61	1.013							1.01	0.41	-9.660
70.05	0.57	0.946							0.95	0.38	-9.822
77.15	0.53	0.880							0.88	0.35	-9.991
85.15	0.49	0.813							0.81	0.33	-10.168
94.25	0.43	0.714							0.71	0.29	-10.400
104.55	0.38	0.631							0.63	0.25	-10.628
120	0.20	0.332							0.33	0.13	-11.407
134	0.46	0.764							0.76	0.31	-10.685
148	0.20	0.332							0.33	0.13	-11.603
164	0.13	0.216							0.22	0.09	-12.150
185.5	0.09	0.149							0.15	0.06	-12.641
210	0.06	0.100							0.10	0.04	-13.171
238.5	0.03	0.050							0.05	0.02	-13.991
271.5	0.01	0.017							0.02	0.01	-15.223
312.5	0.01	0.017							0.02	0.01	-15.360
359	0	0.000							0.00	0.00	ERR
SUM	38.99	64.7234	0	28.993	0	13.984	29.66	147.6748	59.32153		

FIGURE A-12

PLANT 700B, RUN 42, PERIOD B TOTAL PRODUCTS

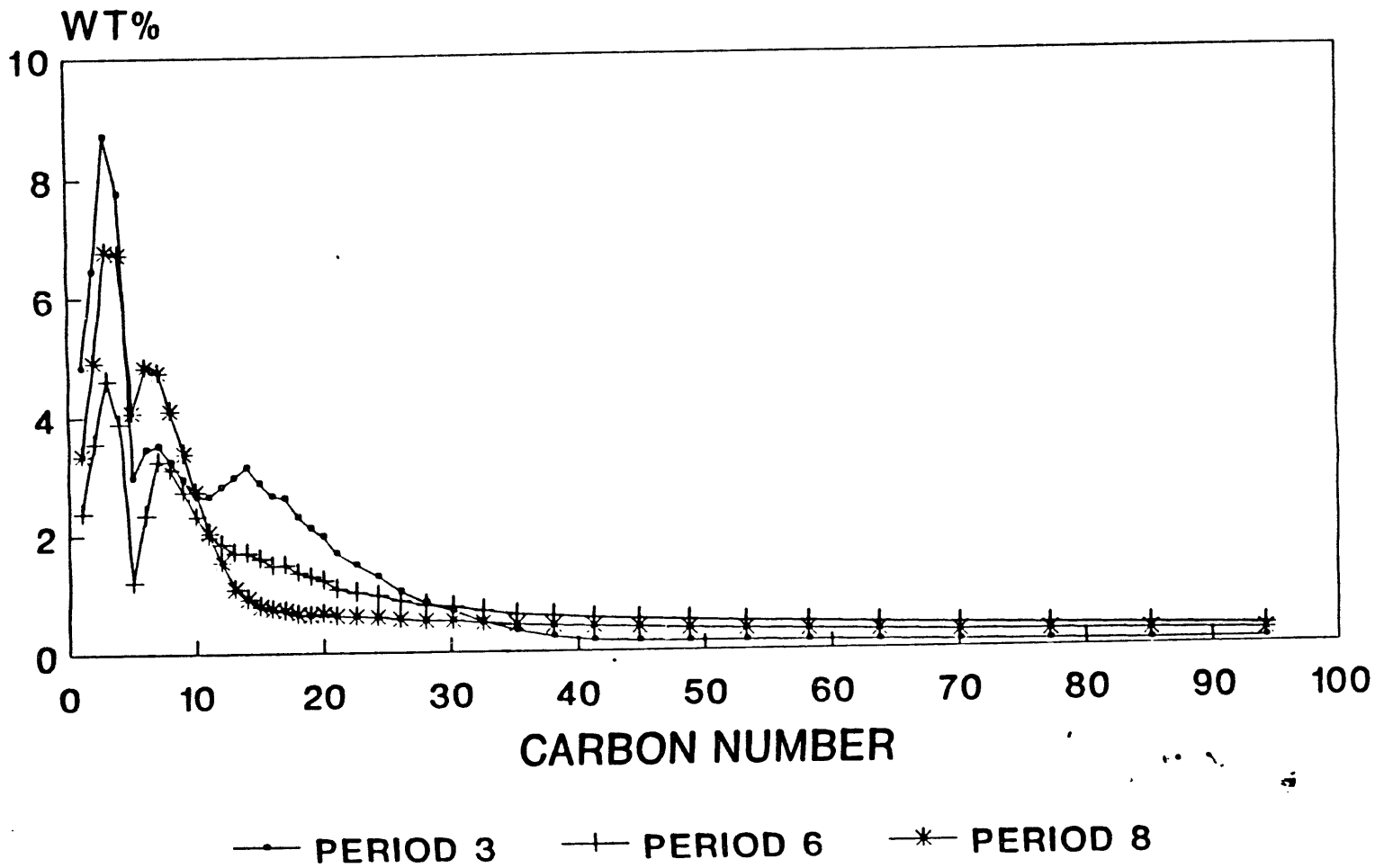
C #	WAX wt%	WAX Gram	ICE AQ Gram	ICE HC Gram	CRYO AQ Gram	CYRO HC Gram	GAS Gram	SUM Gram	WT%	Ln(WT%/CN)	
Total	100	61	0	22.99	0	13	19.17	116.16			
1	0	0.000	0	0	0	0	3.89	3.88	3.34	-3.399	
2	0	0.000	0	0.6	0	0.655	4.45	5.71	4.91	-3.707	
3	0	0.000	0	0.979	0	0.638	6.27	7.89	6.79	-3.788	
4	0	0.000	0	1.64	0	1.621	4.57	7.83	6.74	-4.083	GAS
											21.78
5	0	0.000	0	1.93	0	2.8		4.73	4.07	-4.810	
6	0.04	0.024	0	2.56	0	3		5.58	4.81	-4.827	
7	0.22	0.134	0	3.32		2.03		5.48	4.72	-4.999	
8	0.27	0.165		3.47		1.13		4.76	4.10	-5.273	
9	0.59	0.360		2.97		0.573		3.90	3.36	-5.590	

FIGURE A-12 (CONT)

10	1.07	0.653	2.18	0.327	3.16	2.72	-5.907	
11	1.24	0.756	1.45	0.147	2.35	2.03	-6.297	
12	1.3	0.793	0.916	0.065	1.77	1.53	-6.667	GASOLINE
								27.34
13	1.29	0.787	0.442	0.016	1.24	1.07	-7.101	
14	1.37	0.836	0.221	0	1.06	0.91	-7.339	
15	1.28	0.781	0.126	0	0.91	0.78	-7.561	
16	1.23	0.750	0.095		0.85	0.73	-7.696	
17	1.23	0.750	0.063		0.81	0.70	-7.795	
18	1.17	0.714	0.031		0.74	0.64	-7.940	
19	1.2	0.732	0		0.73	0.63	-8.011	DIESEL
								5.46
20	1.25	0.763	0		0.76	0.66	-8.022	
21.05	1.17	0.714			0.71	0.61	-8.139	HEAVY
22.6	1.16	0.708			0.71	0.61	-8.219	45.42
24.25	1.14	0.695			0.70	0.60	-8.307	
26.05	1.06	0.647			0.65	0.56	-8.451	
28.05	1.01	0.616			0.62	0.53	-8.573	
30.2	1.01	0.616			0.62	0.53	-8.647	
32.55	0.94	0.573			0.57	0.49	-8.794	
35.2	0.86	0.525			0.52	0.45	-8.961	
38.1	0.83	0.506			0.51	0.44	-9.076	
41.3	0.79	0.482			0.48	0.41	-9.206	
44.85	0.75	0.458			0.46	0.39	-9.340	
48.8	0.70	0.427			0.43	0.37	-9.494	
53.25	0.66	0.403			0.40	0.35	-9.640	
58.2	0.63	0.384			0.38	0.33	-9.775	
63.75	0.59	0.360			0.36	0.31	-9.932	
70.05	0.54	0.329			0.33	0.28	-10.115	
77.15	0.52	0.317			0.32	0.27	-10.249	
85.15	0.47	0.287			0.29	0.25	-10.449	
94.25	0.43	0.262			0.26	0.23	-10.639	
104.55	0.40	0.244			0.24	0.21	-10.815	
120	0.22	0.134			0.13	0.12	-11.551	
134	0.55	0.336			0.34	0.29	-10.745	
146	0.27	0.165			0.16	0.14	-11.542	
164	0.20	0.122			0.12	0.11	-11.959	
185.5	0.15	0.092			0.09	0.08	-12.369	
210	0.10	0.061			0.06	0.05	-12.899	
238.5	0.06	0.037			0.04	0.03	-13.537	
272.5	0.04	0.024			0.02	0.02	-14.076	
312.5	0.02	0.012			0.01	0.01	-14.906	
359	0.01	0.006			0.01	0.01	-15.738	
SUM	32.03	19.5383	0	22.993	0	13.002	19.17	74.7033	64.31069

FIGURE A-13

TOTAL HC PRODUCT DISTRIBUTION
PLANT 700B, RUN 42



\RUN42\TOTAL.CHT

FIGURE A-14

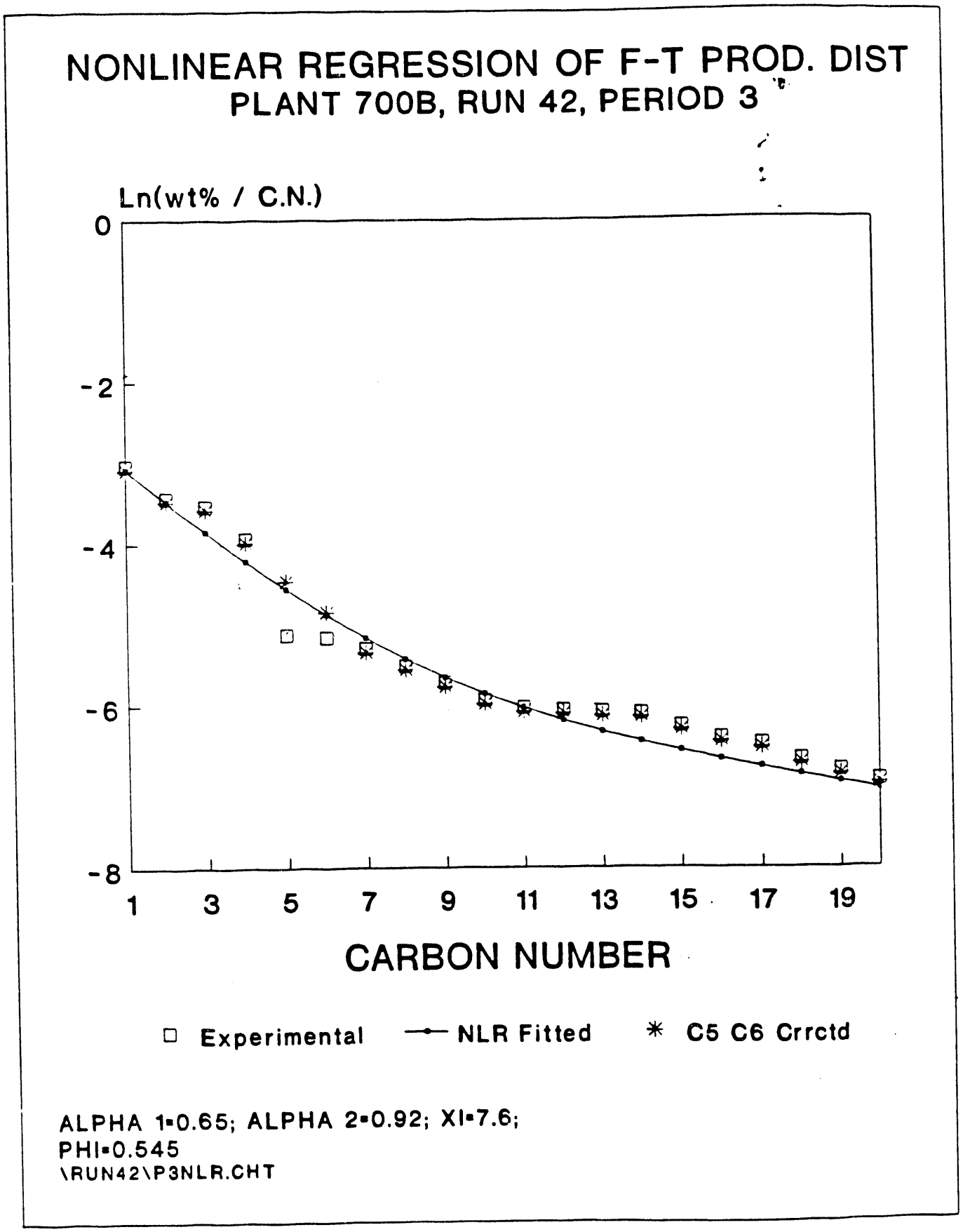

NONLINEAR REGRESSION OF F-T PROD. DIST
PLANT 700B, RUN 42, PERIOD 3
Ln(wt% / C.N.)
0
-2
-4
-6
-8
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
C5 C6 Crrctd
ALPHA 1=0.65; ALPHA 2=0.92; XI=7.6;
PHI=0.545
\RUN42\P3NLR.CHT

FIGURE A-15

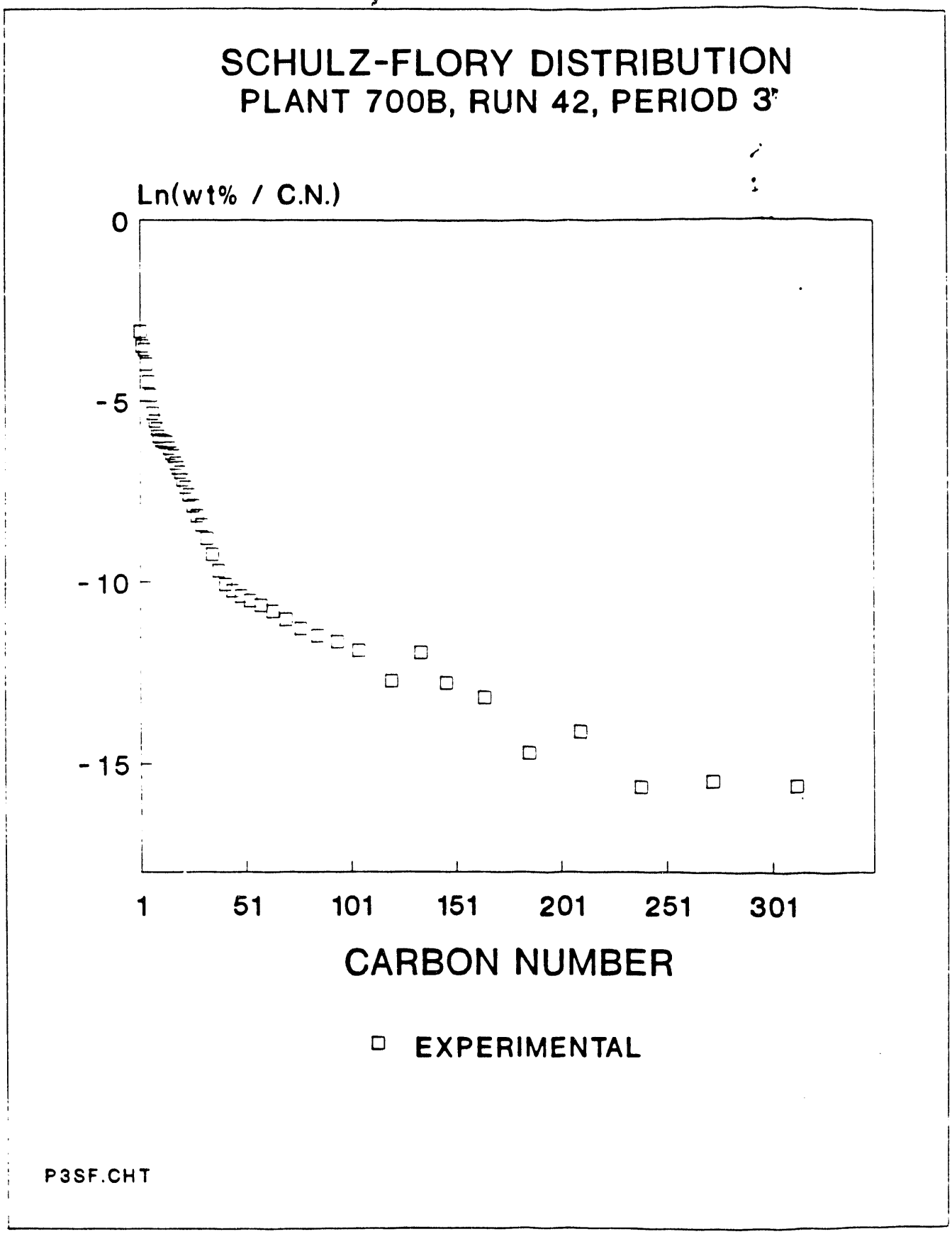

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 42, PERIOD 3
Ln(wt% / C.N.)
0
-5
-10
-15
1
51
101
151
201
251
301
CARBON NUMBER
EXPERIMENTAL
P3SF.CHT

FIGURE A-16

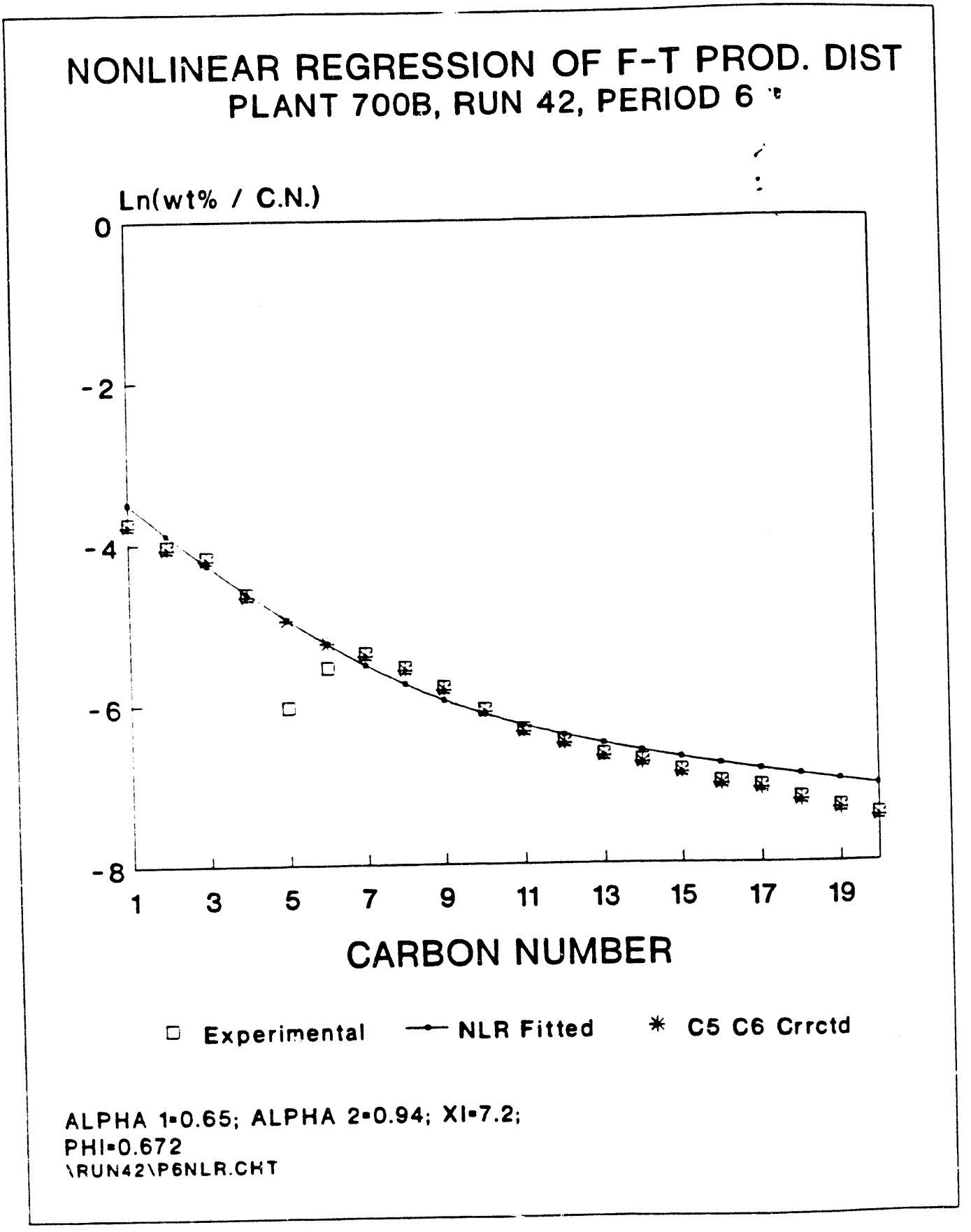

NONLINEAR REGRESSION OF F-T PROD. DIST
PLANT 700B, RUN 42, PERIOD 6
Ln(wt% / C.N.)
0
-2
-4
-6
-8
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
C5 C6 Crrctd
ALPHA 1=0.65; ALPHA 2=0.94; XI=7.2;
PHI=0.672
\RUN42\P6NLR.CHT

FIGURE A-17

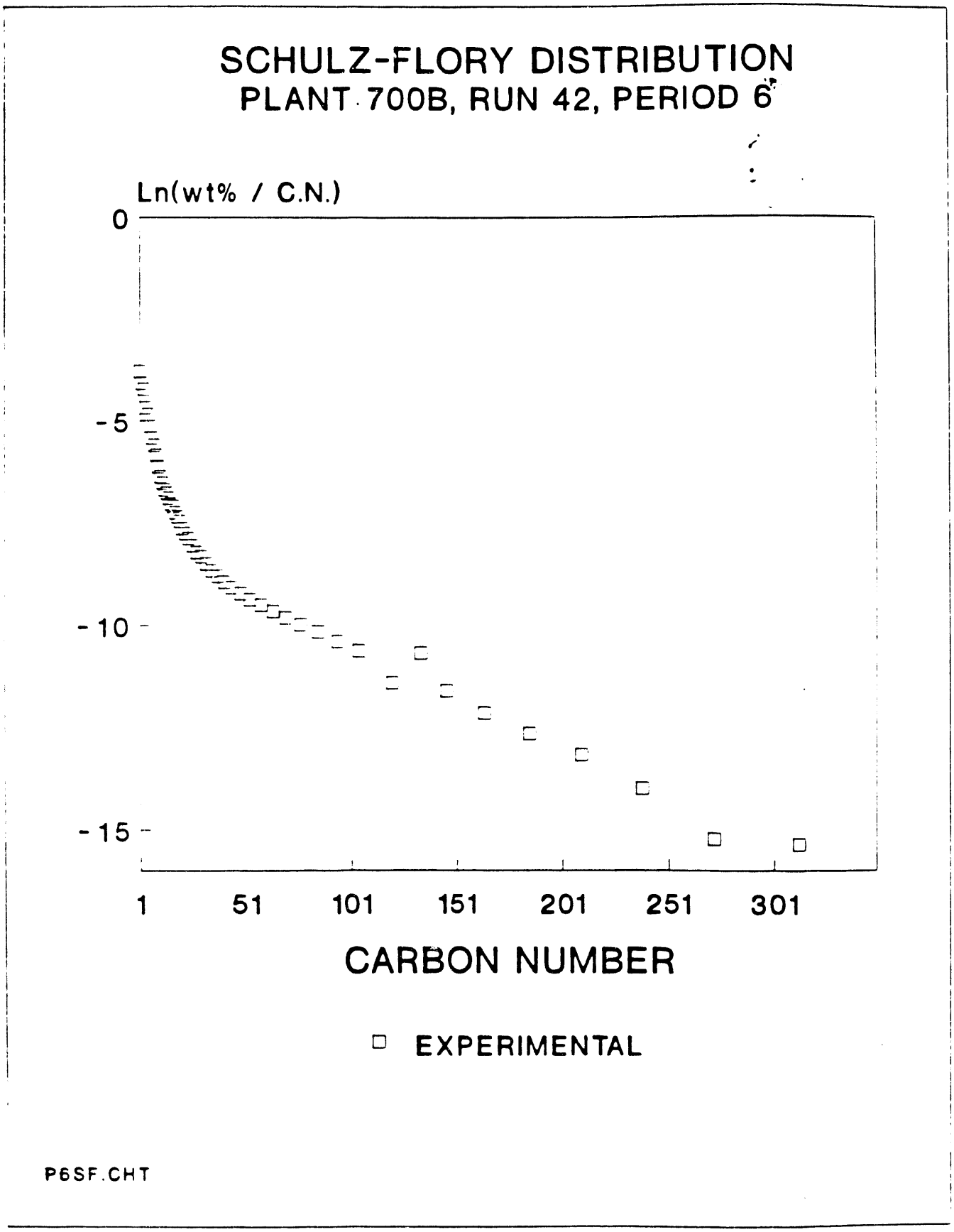

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 42, PERIOD 6
Ln(wt% / C.N.)
0
-5
-10
-15
1
51
101
151
201
251
301
CARBON NUMBER
EXPERIMENTAL
P6SF.CHT

FIGURE A-18

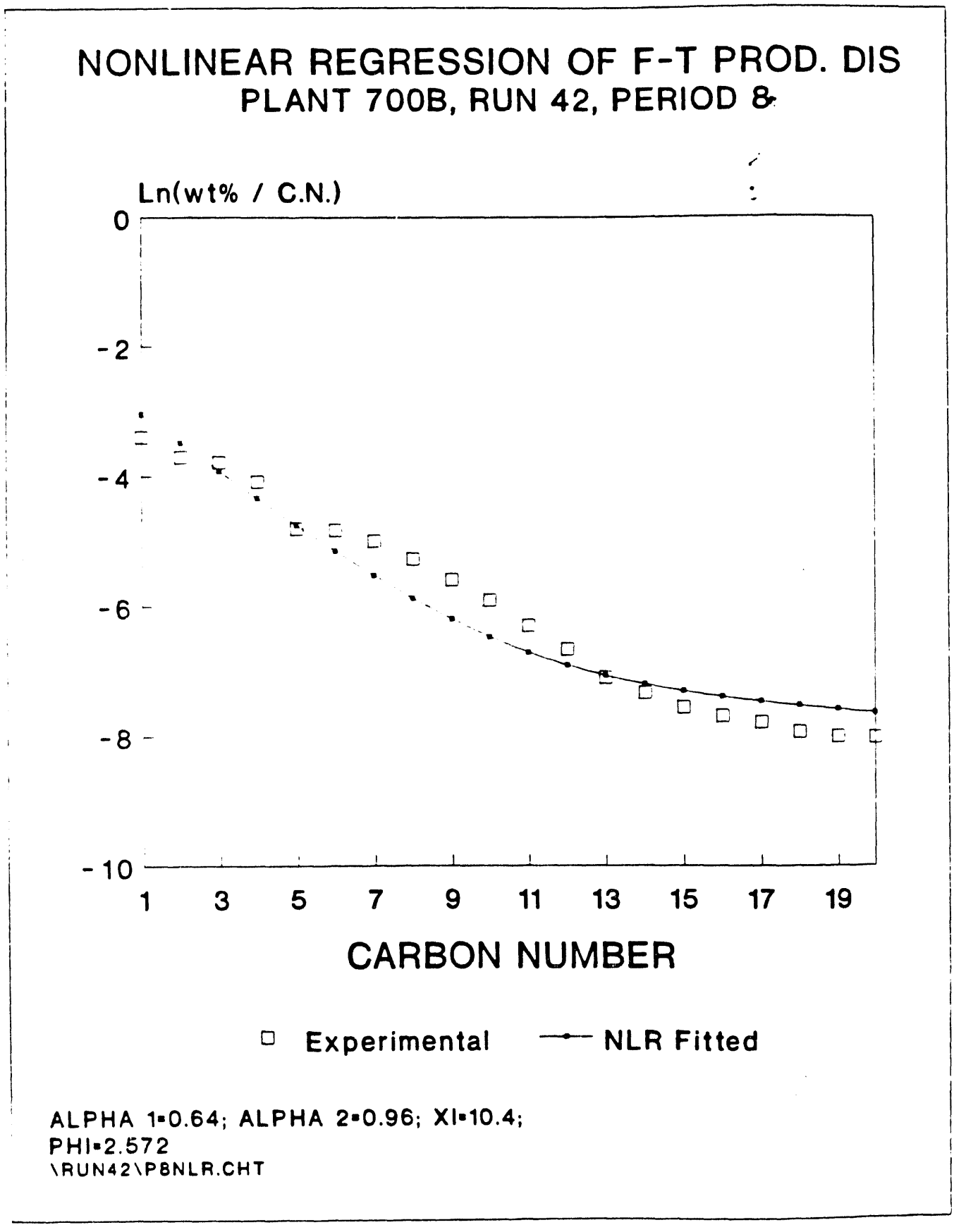

NONLINEAR REGRESSION OF F-T PROD. DIS
PLANT 700B, RUN 42, PERIOD 8
Ln(wt% / C.N.)
0
-2
-4
-6
-8
-10
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
ALPHA 1=0.64; ALPHA 2=0.96; XI=10.4;
PHI=2.572
\RUN42\P8NLR.CHT

FIGURE A-19

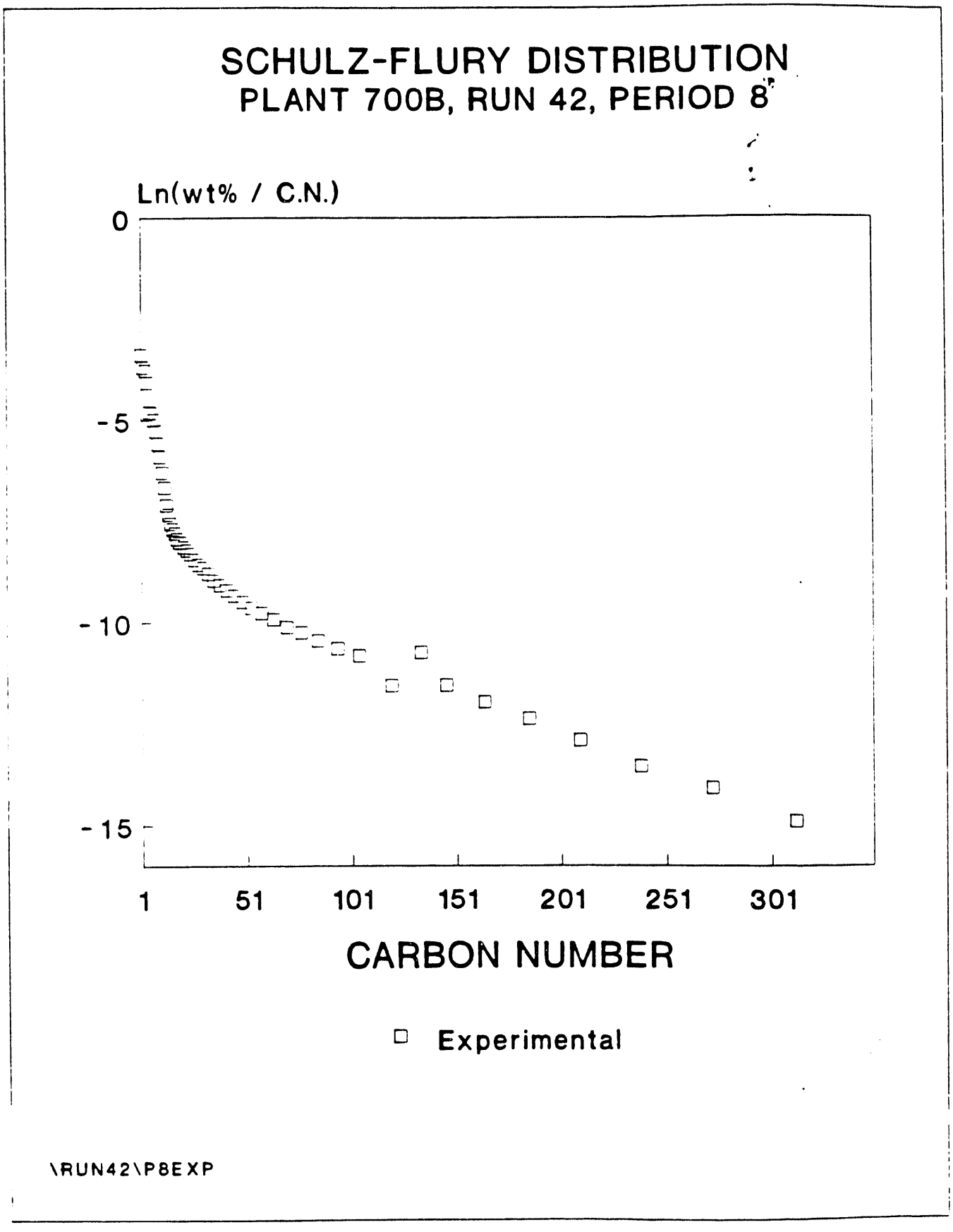
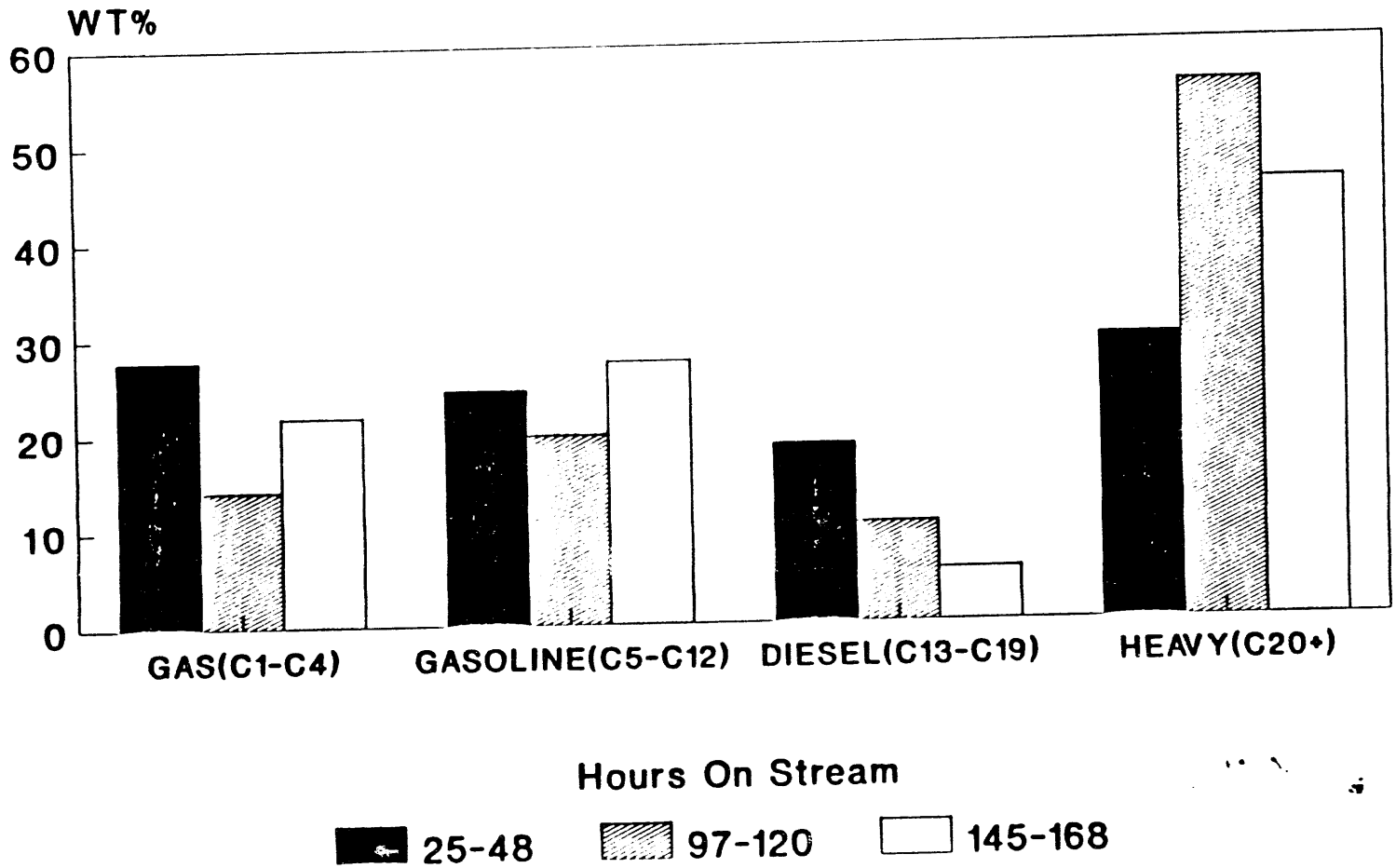

SCHULZ-FLURY DISTRIBUTION
PLANT 700B, RUN 42, PERIOD 8
Ln(wt% / C.N.)
0
-5
-10
-15
1
51
101
151
201
251
301
CARBON NUMBER
Experimental
\RUN42\P8EXP

FIGURE A-20

HC PRODUCT DISTRIBUTION
PLANT 700B RUN 42



\RUN42\GRPDIS.CHT

FIGURE A-21

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K ; 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

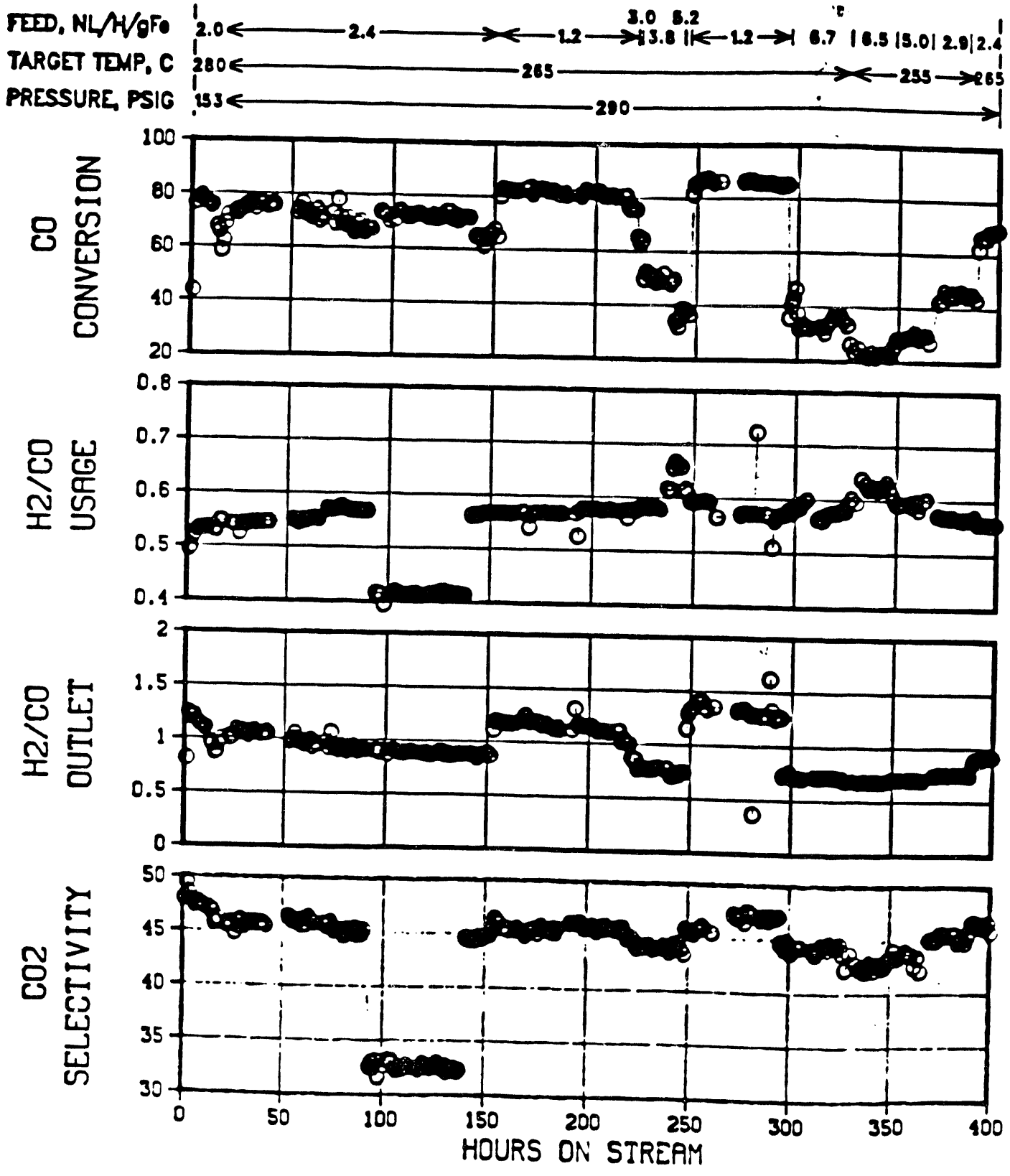


FIGURE A-22

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K ; 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

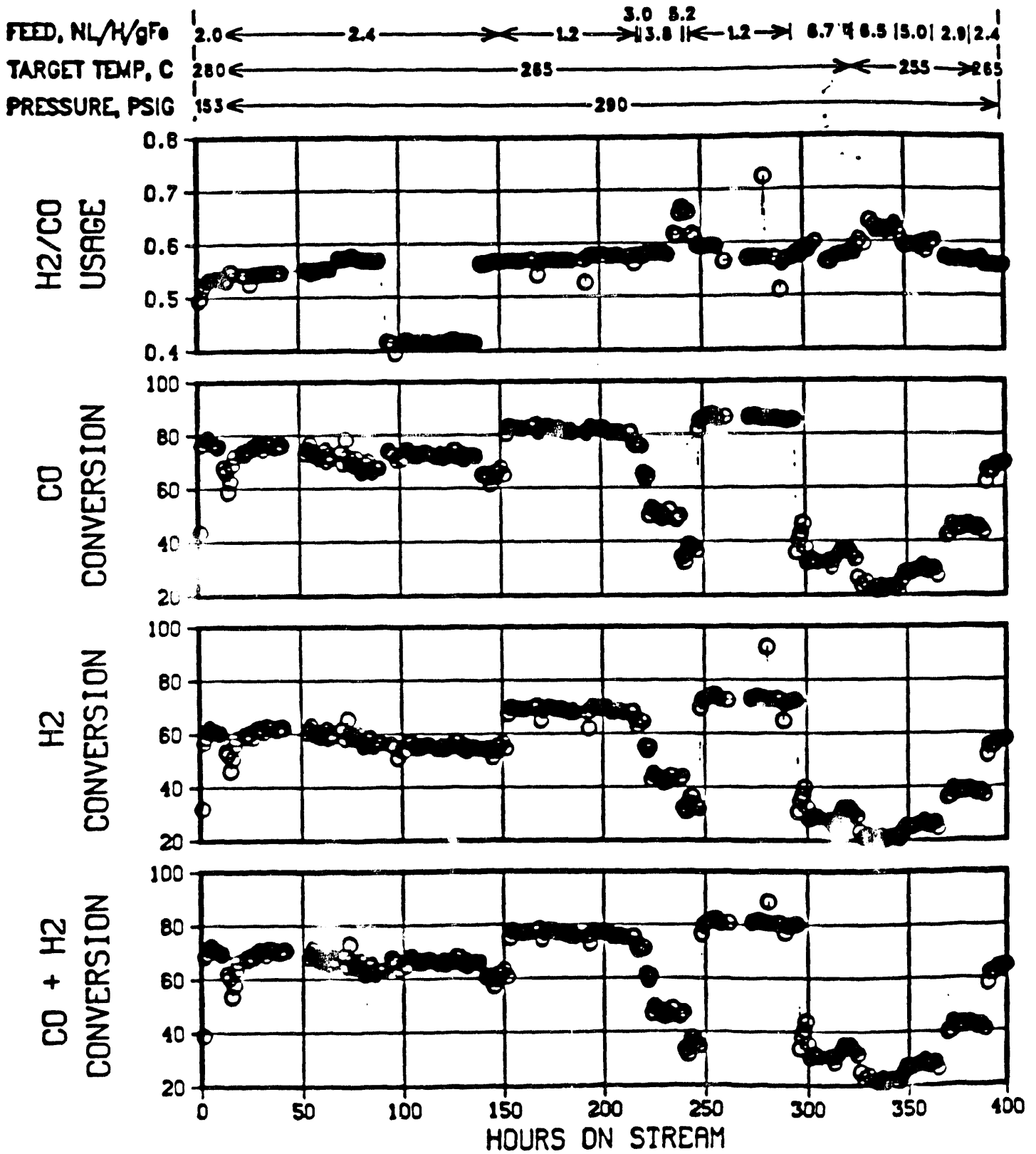


FIGURE A-23

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K ; 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

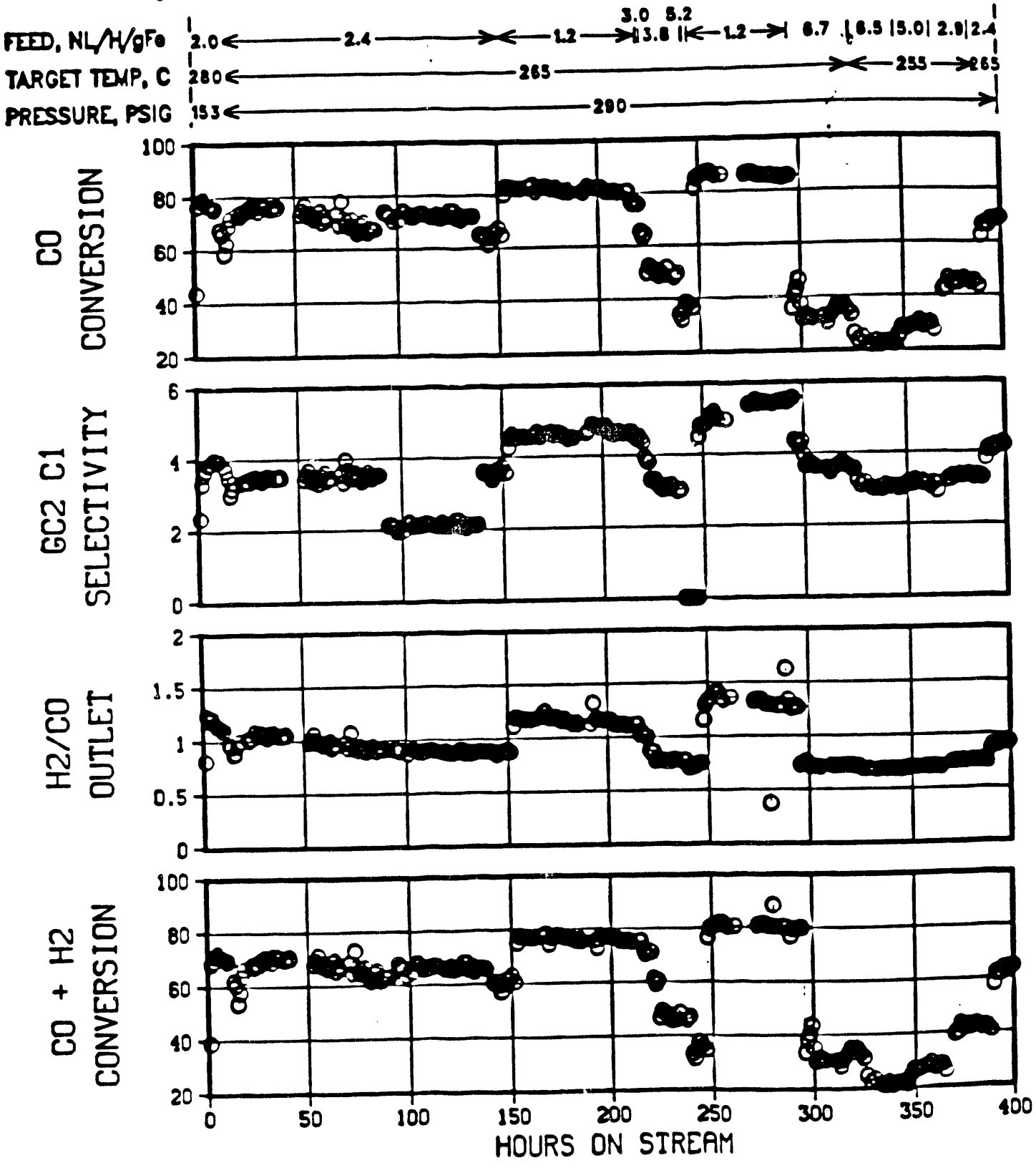


FIGURE A-24

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K ; 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

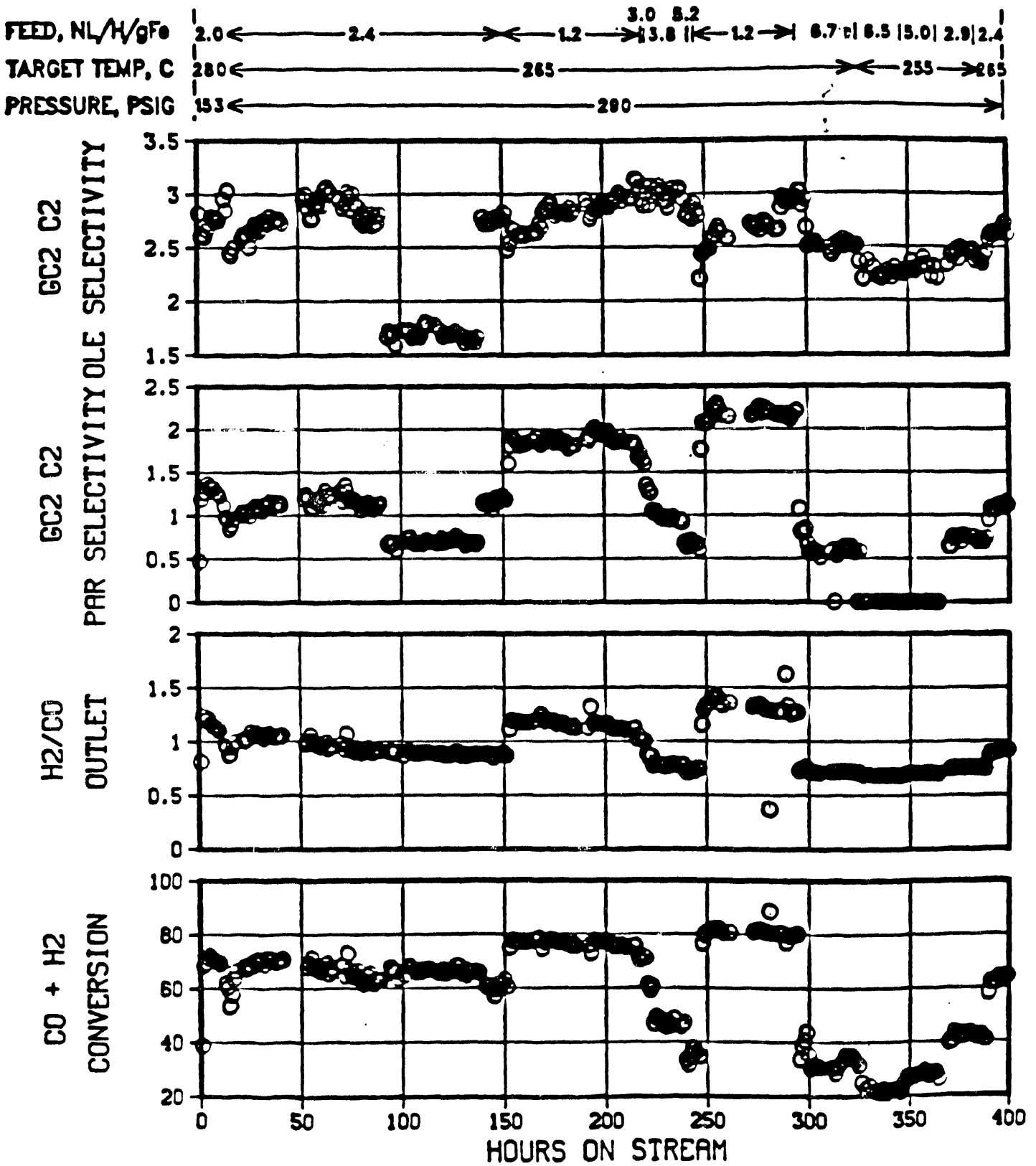


FIGURE A-25

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K ; 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

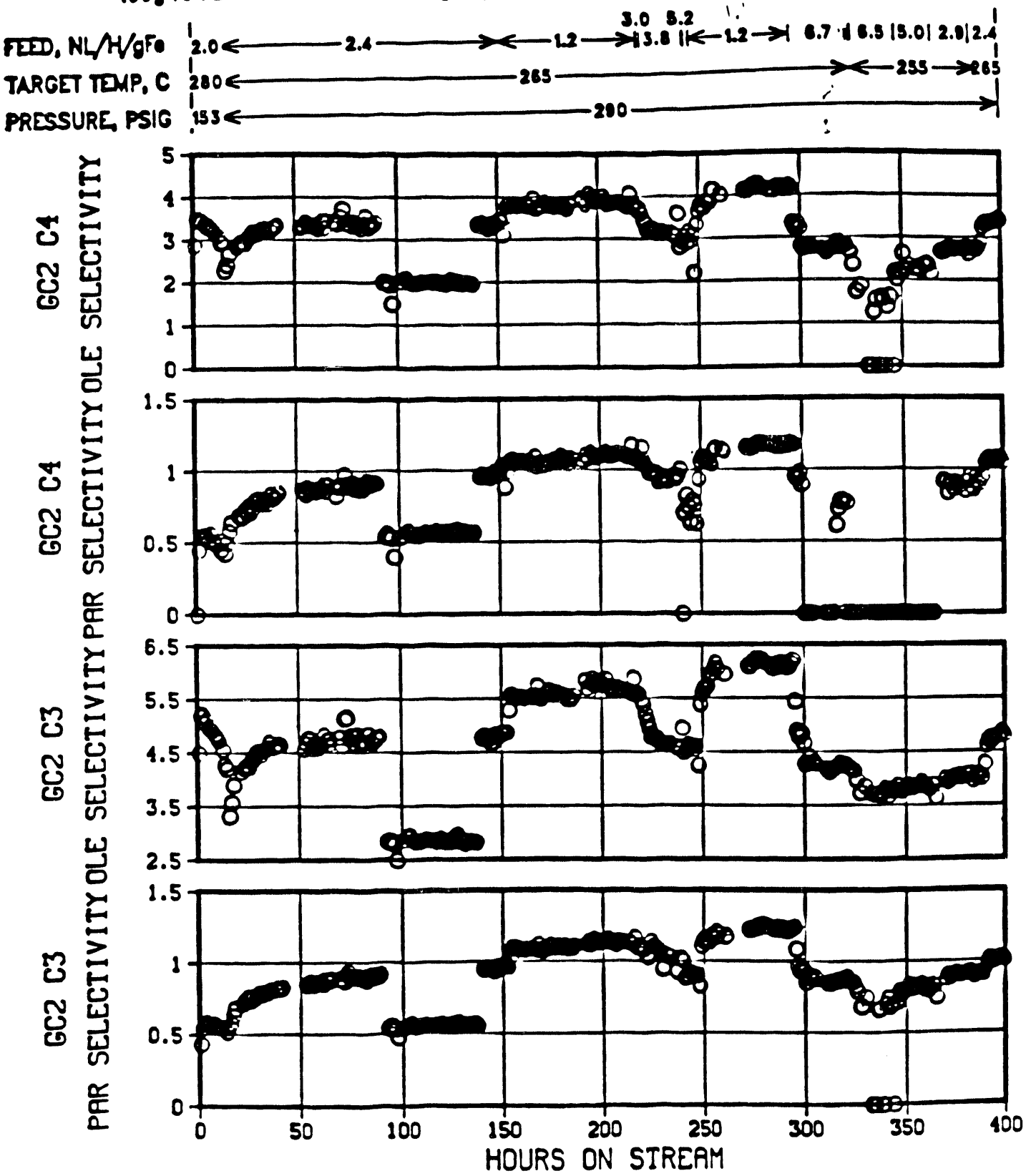


FIGURE A-26

POTASSIUM LAURATE ADDITION TO SLURRY

PLT 700B RUN 43 H_2:CO feed=0.7, 1100 rpm

100g Fe : 2.15 Cu : 2.1 K : 72.7g Fe/Cu Oxide+6.5g K Salt in 290 g C_{30} oil

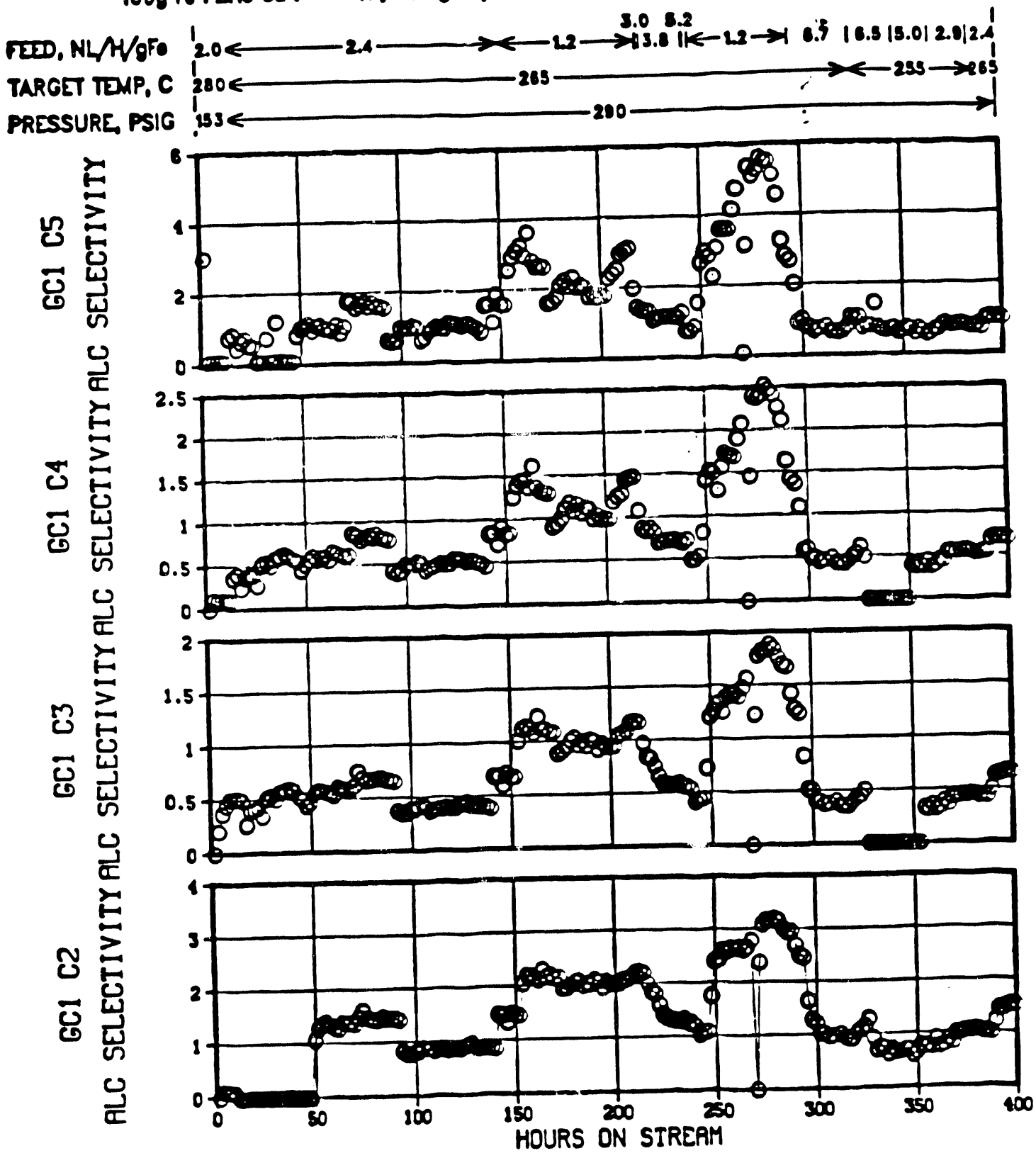


FIGURE A-27

PLANT 700E, RUN 43, PERIOD 4 TOTAL PRODUCTS

C #	MAX wt%	MAX Gram	ICE AD Gram	ICE HC Gram	CRYO AD Gram	CYRO HC Gram	GAS Gram	SUM Gram	WT%	Ln(WT%/CN)
Total		167.64	0	63.99	0	21.98	43.1	296.71		
1	0	0.000	0	0	0	0	9.79	9.79	3.30	-3.411
2	0	0.000	0	3.71	0	1.07	10.08	14.86	5.01	-3.687
3	0	0.000	0	4.36	0	1.04	13.29	18.69	6.30	-3.863
4	0	0.000	0	8.46	0	3.2	9.94	21.62	7.29	-4.005
5	0	0.000	0	7.25	0	5.86		13.13	4.43	-4.727
6	0.2	0.335	0	7.82	0	5.43		13.59	4.58	-4.876
7	1.02	1.710	0	8.73		3.15		13.59	4.58	-5.029
8	1.58	2.649		7.82		1.3		11.77	3.97	-5.307
9	2.35	3.940		6.01		0.416		10.37	3.49	-5.551
10	3.12	5.230		4.04		0.208		9.48	3.19	-5.746
11	3.84	6.437		2.47		0.182		9.09	3.06	-5.884
12	4.29	7.192		1.65		0.104		8.95	3.01	-5.986
13	4.41	7.393		0.824		0.026		8.24	2.78	-6.148
14	4.53	7.594		0.499		0		8.09	2.73	-6.241
15	4.09	6.856		0.247		0		7.10	2.39	-6.440
16	3.68	6.169		0.082		0		6.25	2.11	-6.633
17	3.5	5.867		0				5.87	1.98	-6.757
18	2.98	4.996		0				5.00	1.68	-6.975
19	2.65	4.442		0				4.44	1.50	-7.146
20	2.37	3.973						3.97	1.34	-7.309
21.05	1.91	3.202						3.20	1.08	-7.576
22.6	1.66	2.783						2.78	0.94	-7.787
24.25	1.50	2.515						2.51	0.85	-7.959
26.05	1.29	2.163						2.16	0.73	-8.181
28.05	1.12	1.878						1.88	0.63	-8.397
30.2	1.04	1.743						1.74	0.59	-8.545
32.55	0.89	1.492						1.49	0.50	-8.775
35.2	0.78	1.308						1.31	0.44	-8.986
38.1	0.73	1.224						1.22	0.41	-9.131
41.3	0.64	1.073						1.07	0.36	-9.343
44.85	0.59	0.989						0.99	0.33	-9.507
48.8	0.54	0.905						0.91	0.31	-9.680
53.25	0.49	0.821						0.82	0.28	-9.864
58.2	0.46	0.771						0.77	0.26	-10.017
63.75	0.42	0.704						0.70	0.24	-10.199
70.05	0.37	0.620						0.62	0.21	-10.420
77.15	0.32	0.536						0.54	0.18	-10.661
85.15	0.27	0.453						0.45	0.15	-10.930
94.25	0.23	0.386						0.39	0.13	-11.192
104.55	0.19	0.319						0.32	0.11	-11.487

FIGURE A-27 (CONT)

120	0.10	0.168						0.17	0.06	-12.266
134	0.21	0.352						0.35	0.12	-11.635
146	0.09	0.151						0.15	0.05	-12.568
164	0.05	0.084						0.08	0.03	-13.272
185.5	0.04	0.067						0.07	0.02	-13.618
216	0.02	0.034						0.03	0.01	-14.435
238.5	0.01	0.017						0.02	0.01	-15.256
272.5	0.01	0.017						0.02	0.01	-15.389
312.5	0	0.000						0.00	0.00	ERR
359	0	0.000						0.00	0.00	ERR
SUM	60.58	101.5563	0	63.992	0	22.006	43.1	230.6543	77.73728	

FIGURE A-28

PLANT 70[illegible], RUN 4[illegible], PERIOD 9 TOTAL PRODUCTS

C #	WAY Wt%	WAX Gram	ICE AO Gram	ICE HC Gram	OFVC AO Gram	OVFC HC Gram	GAS Gram	SUM Gram	WT%	LN(WT%/CN
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

FIGURE A-28 (CONT)

85.75	0.4[illegible]	0.17[illegible]							0.17	0.12	-11.170
6[illegible].2[illegible]	0.34	0.14[illegible]							0.15	0.10	-11.435
10[illegible].[illegible]	0.2[illegible]	0.124							0.12	0.09	-11.697
12[illegible]	0.1[illegible]	0.064							0.06	0.04	-12.494
134	0.34	0.146							0.15	0.10	-11.786
146	0.15	0.064							0.06	0.04	-12.690
164	0.10	0.043							0.04	0.03	-13.212
185.5	0.07	0.030							0.03	0.02	-13.692
210	0.05	0.022							0.02	0.02	-14.113
238.5	0.03	0.013							0.01	0.01	-14.791
272.5	0.02	0.009							0.01	0.01	-15.329
312.5	0.01	0.004							0.00	0.00	-16.160
359	0	0.000							0.00	0.00	ERR

SUM	43.032	18.44480	1.991	44.999	0	20.992	30.13	116.5568 81.52878

FIGURE A-29

PLANT 700E, RUN 43, PERIOD 15 TOTAL PRODUCTS

C #	MAT wt%	MAT Gram	ICE AQ Gram	ICE HC Gram	CRYO AQ Gram	CYRO HC Gram	GAS Gram	SUM Gram	WT%	Ln(WT%/CN)
Total		154.5	1.093	62.99	2.291	18	53.93	292.80		
1	0	0.000	0	0	0	0	16.09	16.09	5.50	-2.901
2	0	0.000	0.719	1.22	1.5	0.781	10.84	15.06	5.14	-3.661
3	0	0.000	0.213	2.69	0.513	0.804	15.06	19.28	6.58	-3.819
4	0	0.000	0.114	4.73	0.196	1.47	8.56	15.07	5.15	-4.353
5	0	0.000	0.047	5.54	0.082	3.03		8.70	2.97	-5.126
6	0.32	0.494	0	5.95	0	3.62		10.06	3.44	-5.162
7	0.4	0.618	0	7.33		2.81		10.76	3.67	-5.250
8	0.83	1.282		8.15		2.44		11.87	4.05	-5.285
9	1.2	1.854		7.66		1.58		11.09	3.79	-5.470
10	1.58	2.441		6.11		0.851		9.40	3.21	-5.741
11	1.78	2.750		4.32		0.378		7.45	2.54	-6.069
12	1.92	2.966		3.5		0.166		6.63	2.27	-6.272
13	2.05	3.167		2.36		0.071		5.60	1.91	-6.522
14	2.21	3.414		1.47		0		4.88	1.67	-6.733
15	2.1	3.245		0.856		0		4.14	1.41	-6.967
16	2.01	3.105		0.57				3.68	1.26	-7.150
17	2.1	3.245		0.326				3.57	1.22	-7.240
18	1.94	2.997		0.162				3.16	1.08	-7.415
19	1.93	2.982						2.98	1.02	-7.531
20	1.94	2.997						3.00	1.02	-7.578
21.25	1.81	2.781						2.78	0.95	-7.704
22.5	1.73	2.677						2.67	0.91	-7.814
23.75	1.69	2.611						2.61	0.89	-7.908
25.25	1.55	2.395						2.39	0.82	-8.066
26.75	1.42	2.194						2.19	0.75	-8.228
28.5	1.39	2.148						2.15	0.73	-8.323
30.25	1.24	1.916						1.92	0.65	-8.512
32.0	1.13	1.746						1.75	0.60	-8.657
33.1	1.08	1.669						1.67	0.57	-8.538
41.0	0.96	1.487						1.48	0.51	-9.006
44.25	0.88	1.361						1.36	0.46	-9.176
48.0	0.79	1.221						1.22	0.42	-9.368
51.25	0.72	1.112						1.11	0.38	-9.548
55.0	0.65	1.004						1.00	0.34	-9.739
63.75	0.58	0.896						0.90	0.31	-9.944
70.25	0.51	0.788						0.79	0.27	-10.167
77.15	0.45	0.695						0.70	0.24	-10.389
85.15	0.39	0.602						0.60	0.21	-10.631
94.25	0.33	0.510						0.51	0.17	-10.899
104.55	0.27	0.417						0.42	0.14	-11.203
127	0.14	0.216						0.22	0.07	-11.998
134	0.31	0.479						0.48	0.16	-11.314
146	0.14	0.216						0.22	0.07	-12.194
164	0.09	0.139						0.14	0.05	-12.752
185.5	0.06	0.093						0.09	0.03	-13.281
210	0.04	0.062						0.06	0.02	-13.810

FIGURE A-29 (CONT)

238.5	0.02	0.031					0.03	0.01	-14.631
272.5	0.01	0.015					0.02	0.01	-15.457
312.5	0.01	0.015					0.02	0.01	-15.594
359	0	0.000					0.00	0.00	ERR
SUM	44.69	69.04605	1.093	62.985	2.291	18.001	50.55	203.9660	69.65958

FIGURE A-30

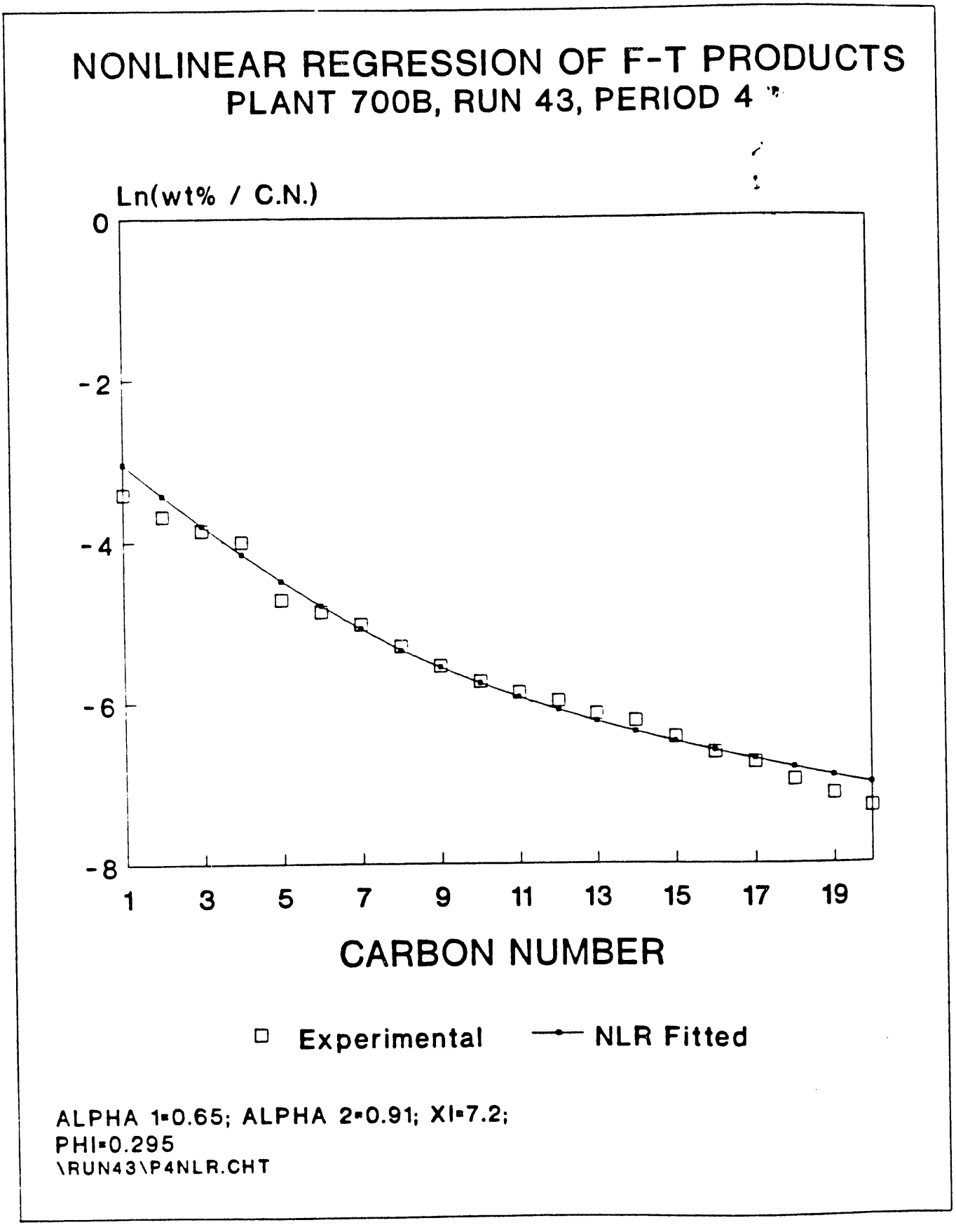

NONLINEAR REGRESSION OF F-T PRODUCTS
PLANT 700B, RUN 43, PERIOD 4
Ln(wt% / C.N.)
0
-2
-4
-6
-8
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
ALPHA 1=0.65; ALPHA 2=0.91; XI=7.2;
PHI=0.295
\RUN43\P4NLR.CHT

FIGURE A-31

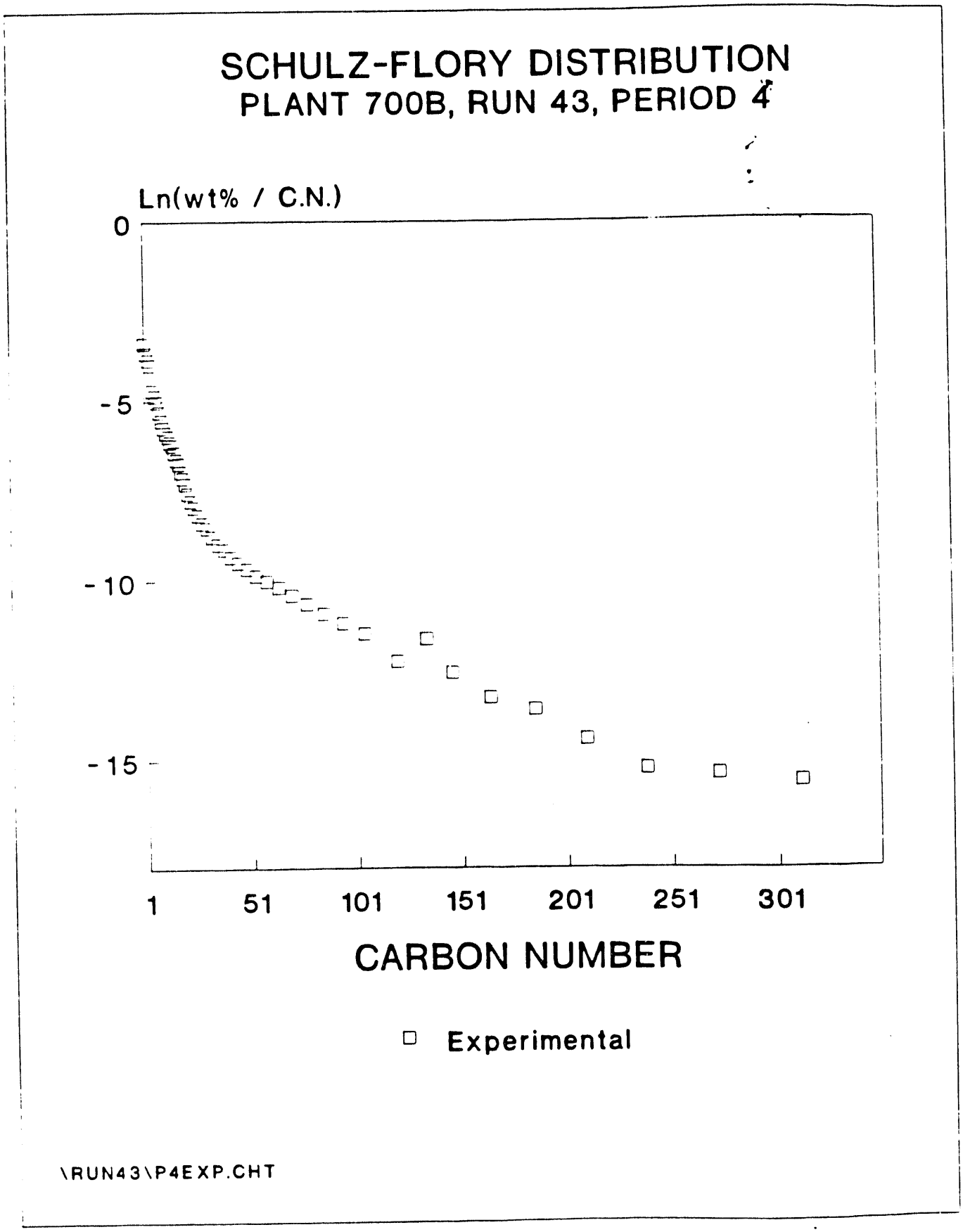

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 4
Ln(wt% / C.N.)
0
-5
-10
-15
1
51
101
151
201
251
301
CARBON NUMBER
Experimental
\RUN43\P4EXP.CHT

FIGURE A-32

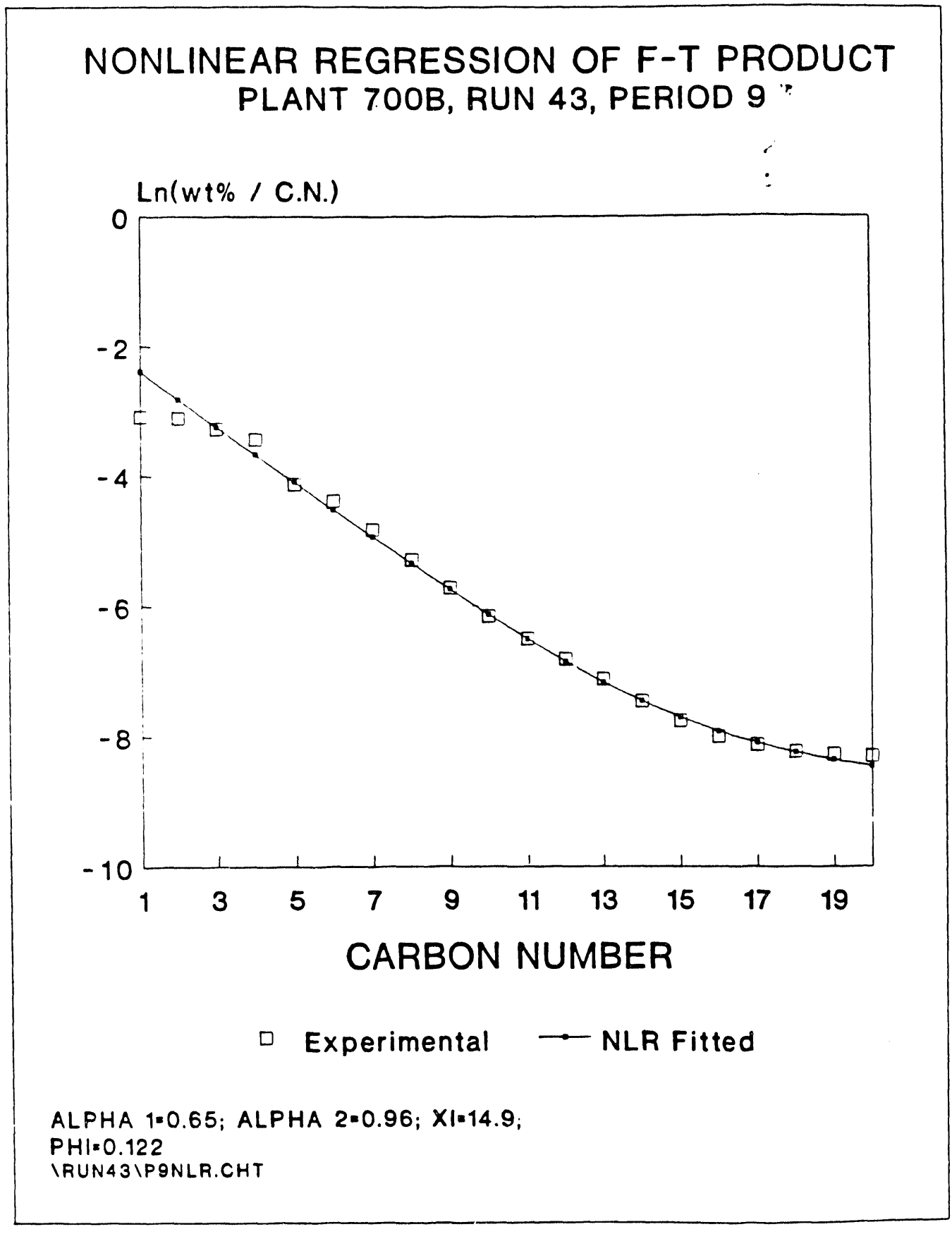

NONLINEAR REGRESSION OF F-T PRODUCT
PLANT 700B, RUN 43, PERIOD 9
Ln(wt% / C.N.)
0
-2
-4
-6
-8
-10
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
ALPHA 1=0.65; ALPHA 2=0.96; XI=14.9;
PHI=0.122
\RUN43\P9NLR.CHT

FIGURE A-33

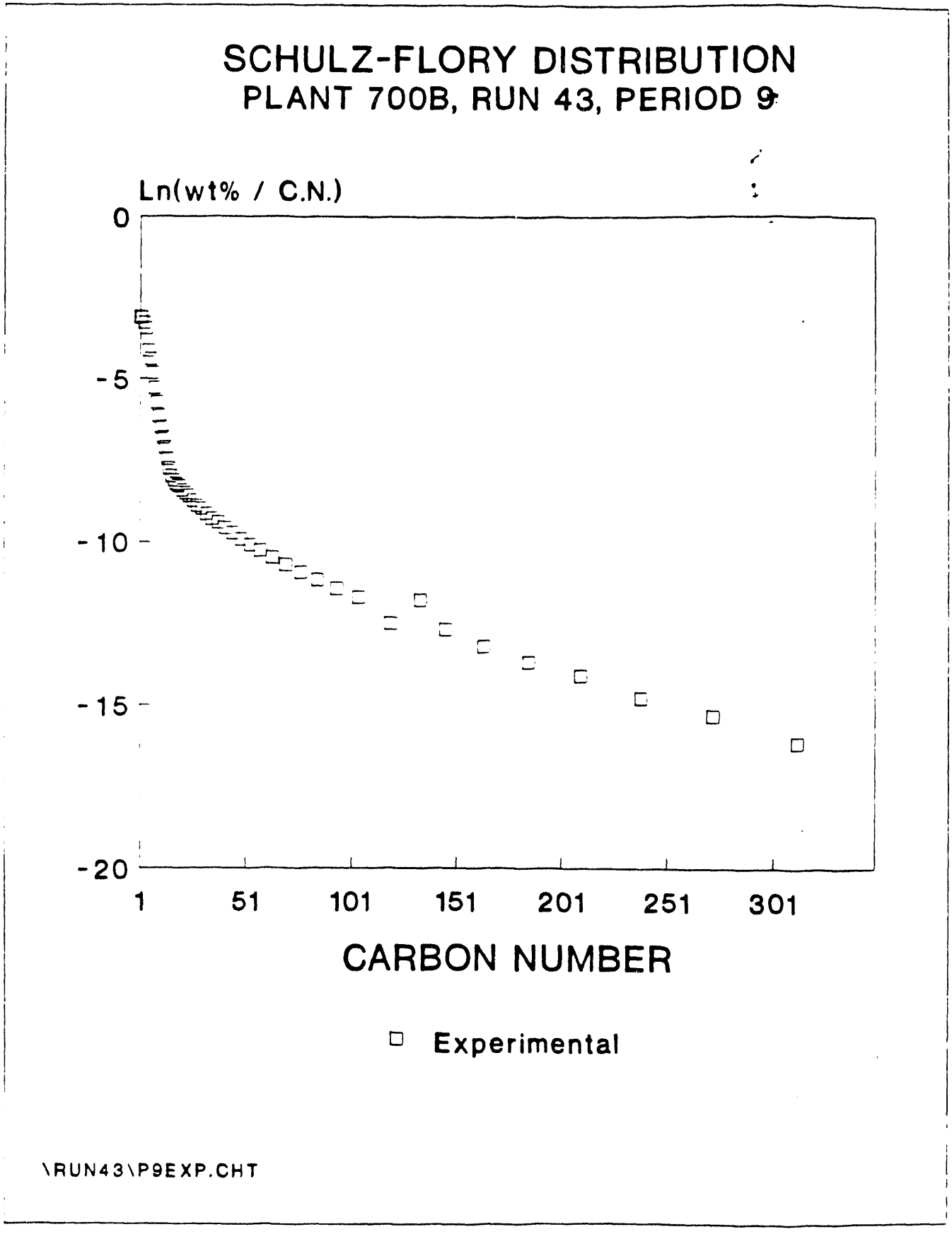

SCHULZ-FLORY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 9
Ln(wt% / C.N.)
0
-5
-10
-15
-20
1
51
101
151
201
251
301
CARBON NUMBER
Experimental
\RUN43\P9EXP.CHT

FIGURE A-34

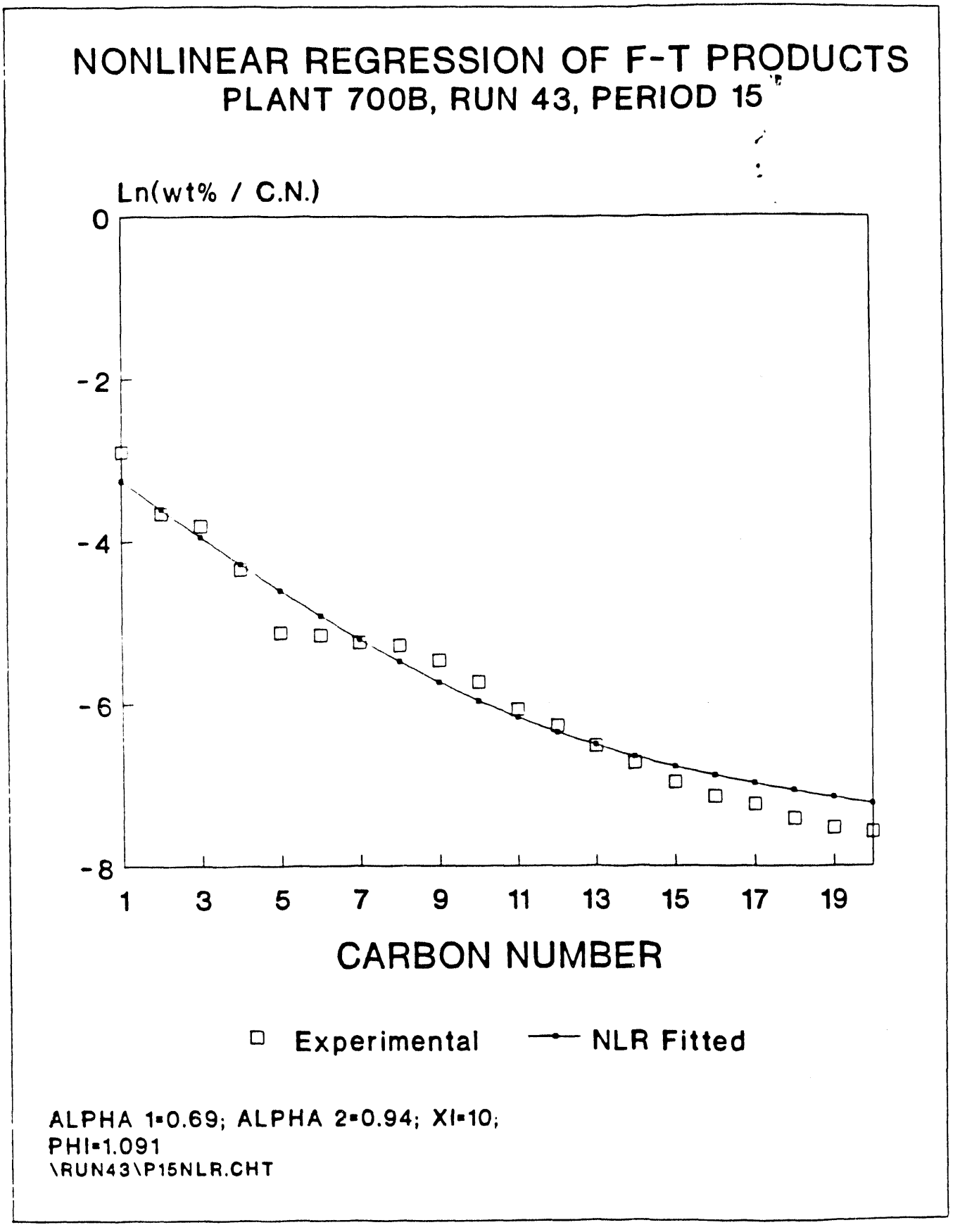

NONLINEAR REGRESSION OF F-T PRODUCTS
PLANT 700B, RUN 43, PERIOD 15
Ln(wt% / C.N.)
0
-2
-4
-6
-8
1
3
5
7
9
11
13
15
17
19
CARBON NUMBER
Experimental
NLR Fitted
ALPHA 1=0.69; ALPHA 2=0.94; XI=10;
PHI=1.091
\RUN43\P15NLR.CHT

FIGURE A-35

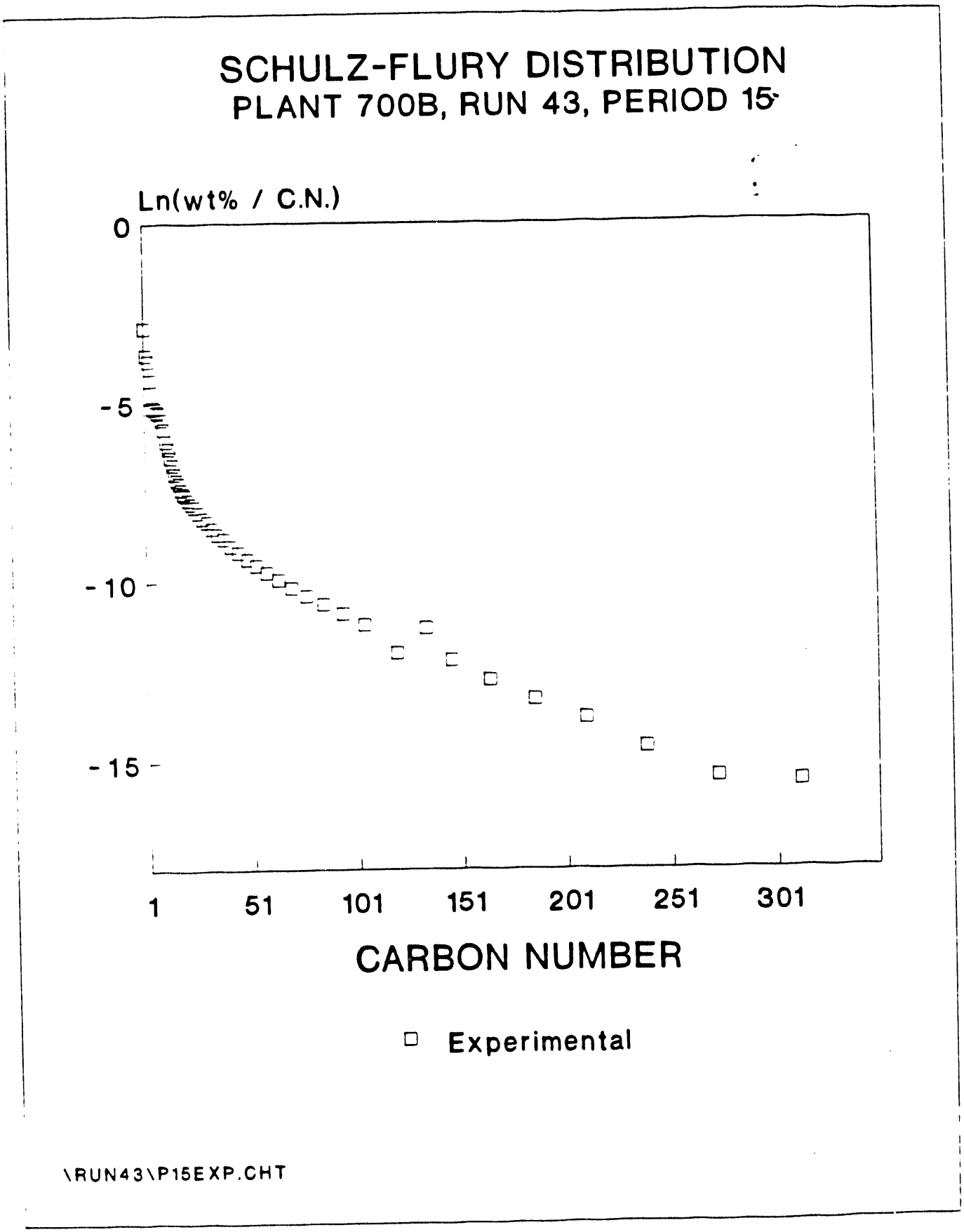
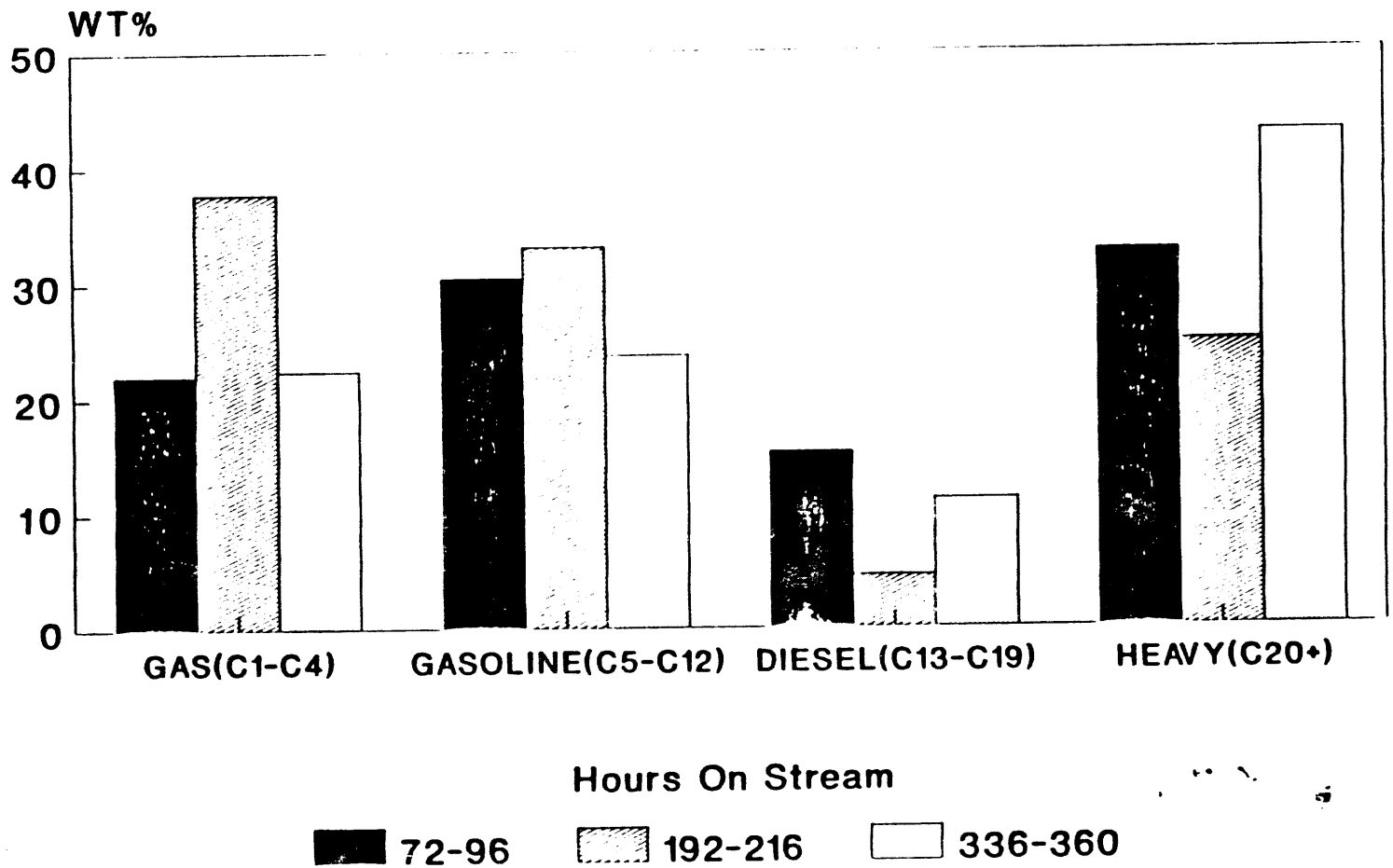

SCHULZ-FLURY DISTRIBUTION
PLANT 700B, RUN 43, PERIOD 15
Ln(wt% / C.N.)
0
-5
-10
-15
1
51
101
151
201
251
301
CARBON NUMBER
Experimental
\RUN43\P15EXP.CHT

FIGURE A-36

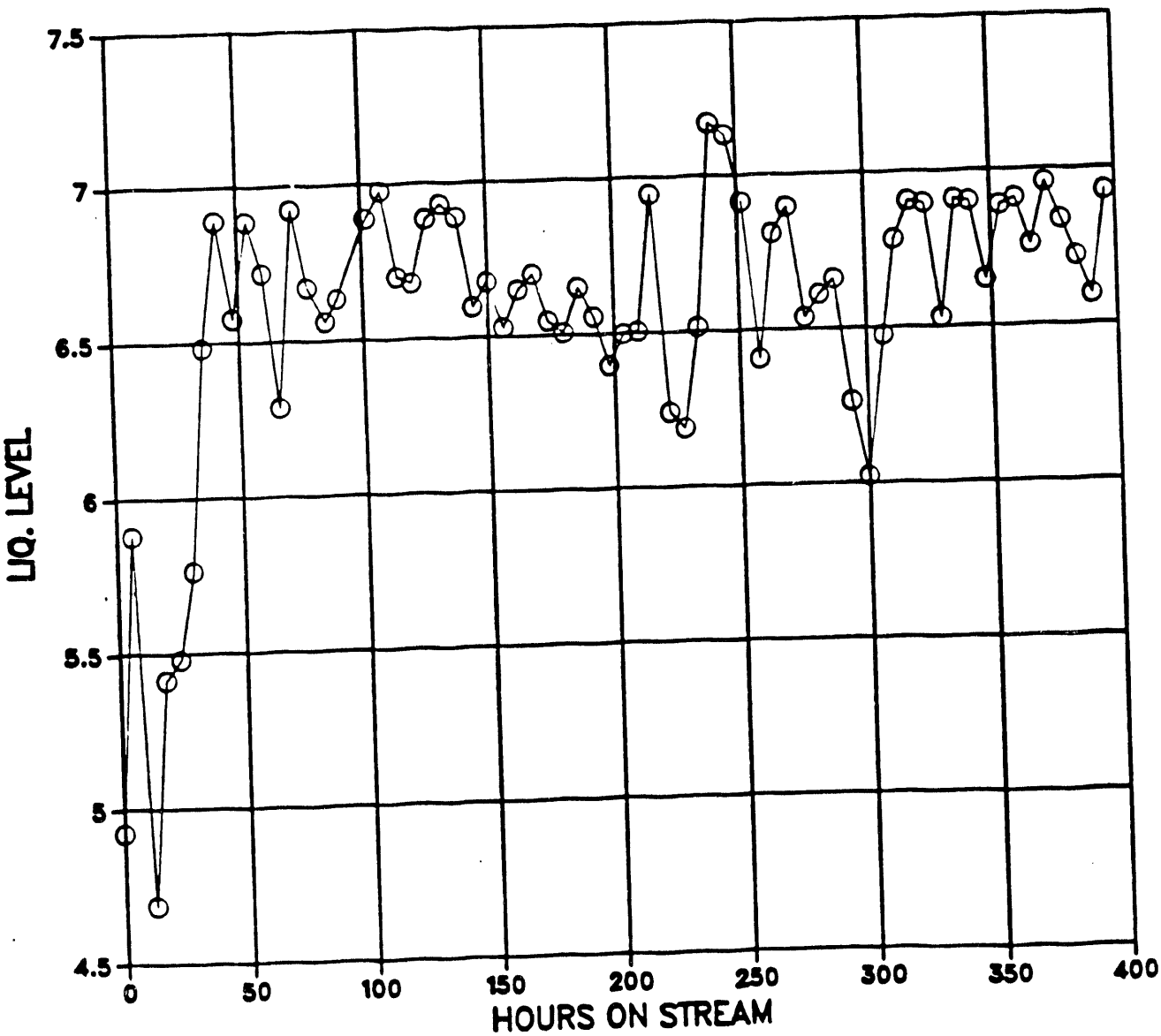
HC PRODUCT DISTRIBUTION
PLANT 700B RUN 43



\RUN43\GRPDIS.CHT

FIGURE A-37

LIQUID LEVEL Vs. HOURS ON STREAM
PLANT 700B RUN 43



[ADAMI.FT]SHOLA.DAT

FIGURE A-38

Plant 700B, Run 43
CO Conv/Methane Selec

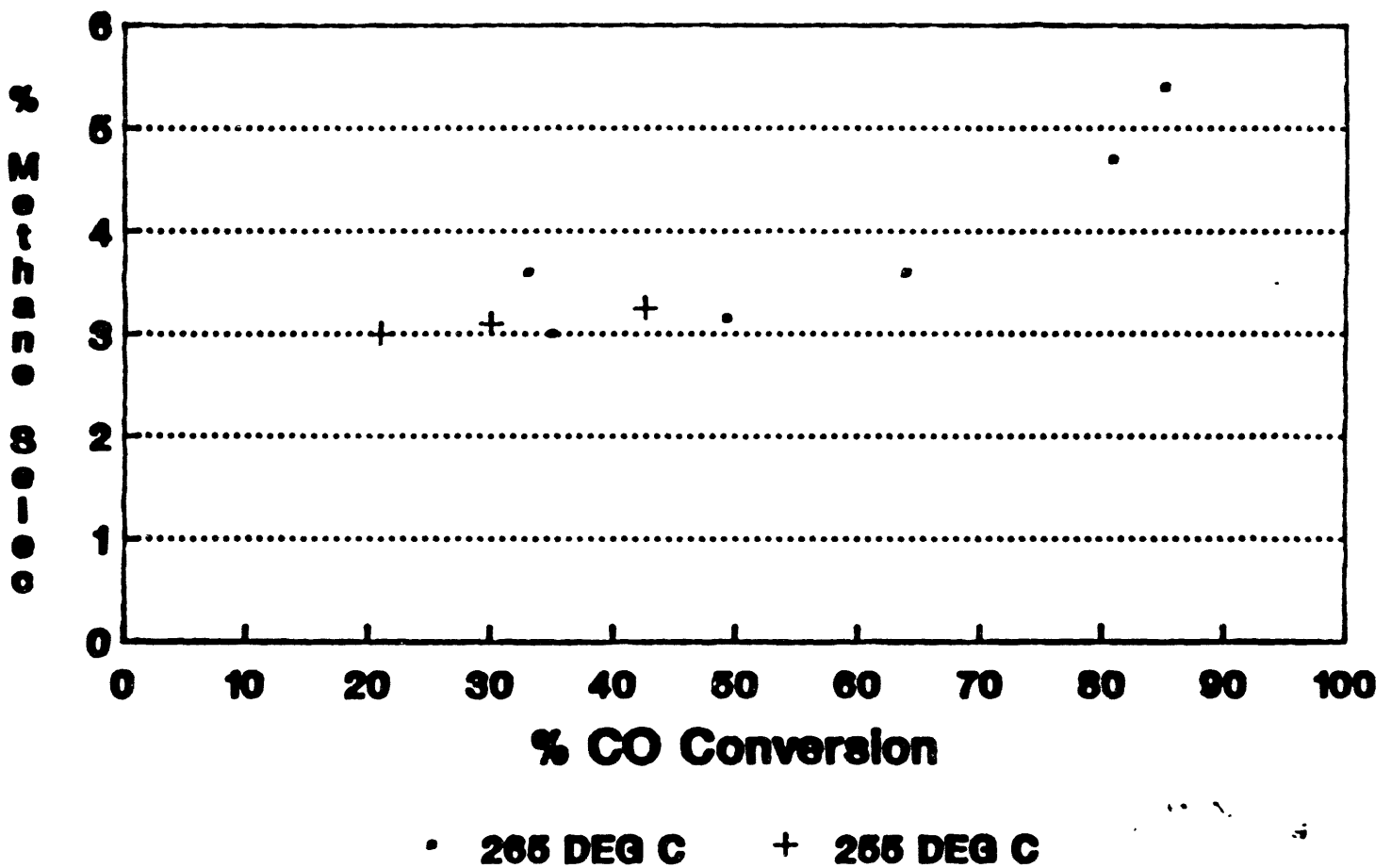


FIGURE A-39

Plant 700B, Run 43
Contact Time/Methane Yield

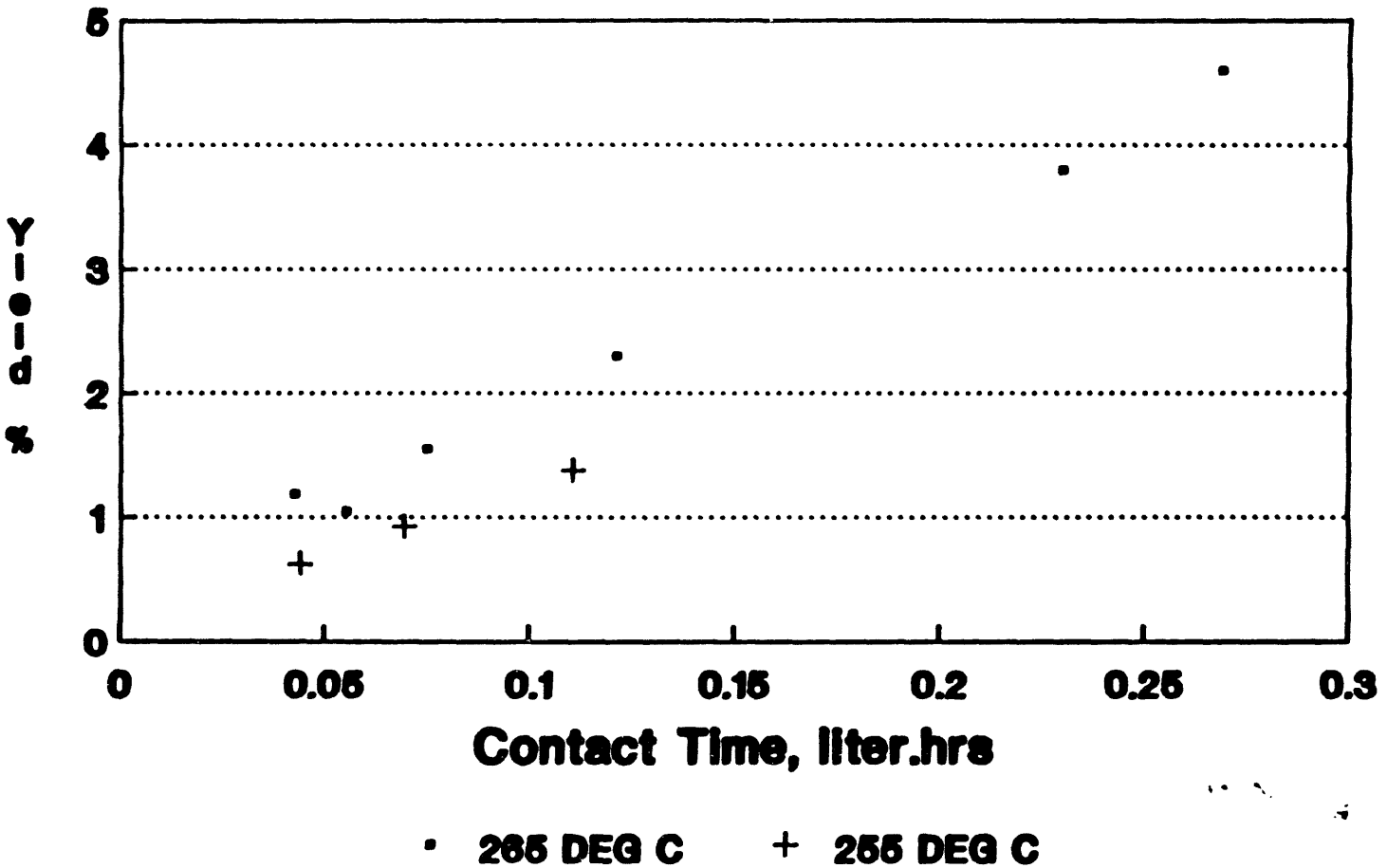


FIGURE A-40

Plant 700B, Run 43
Contact Time/Ethylene Yield

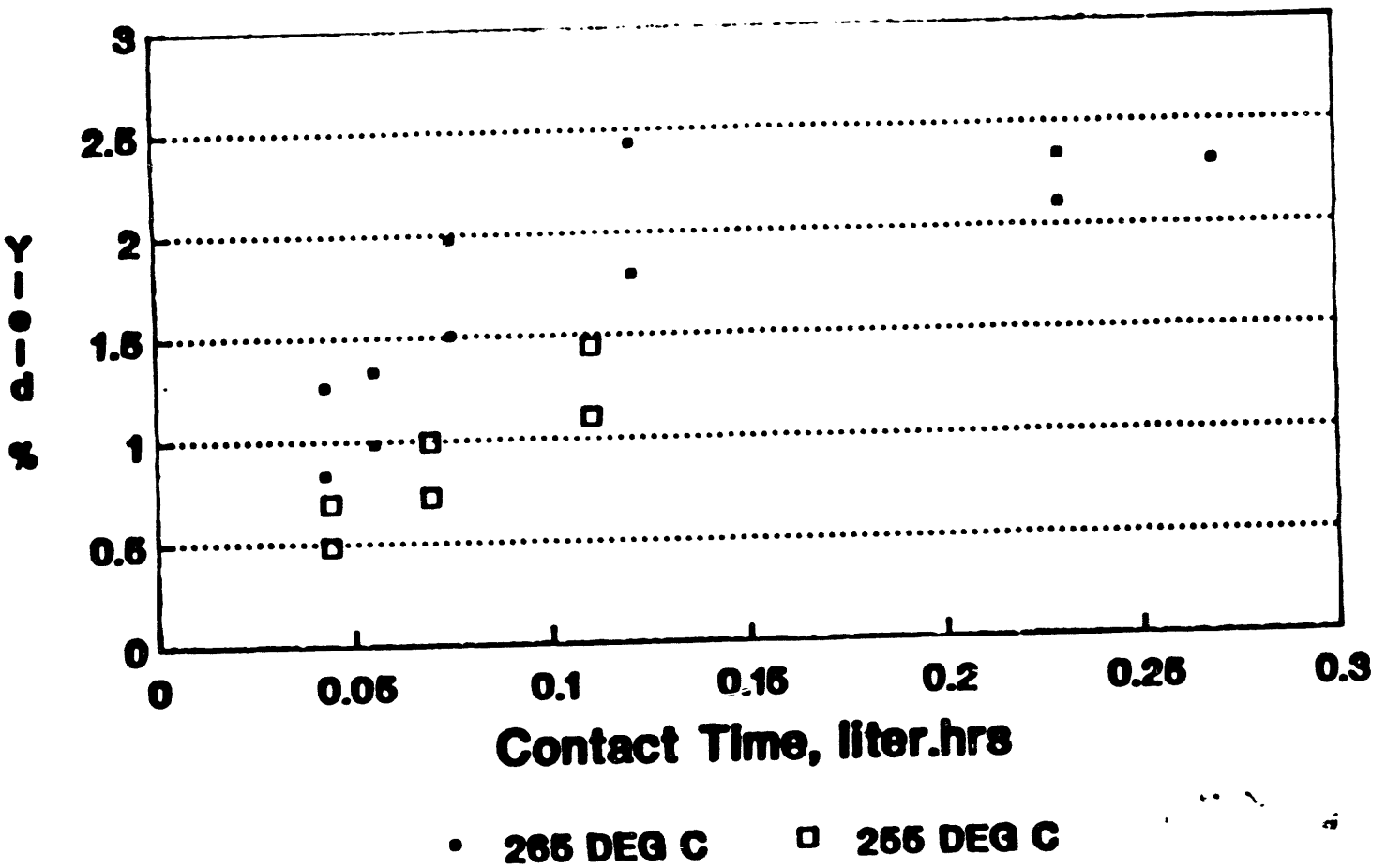


FIGURE A-41

Plant 700B, Run 43
Contact Time/Ethane Yield

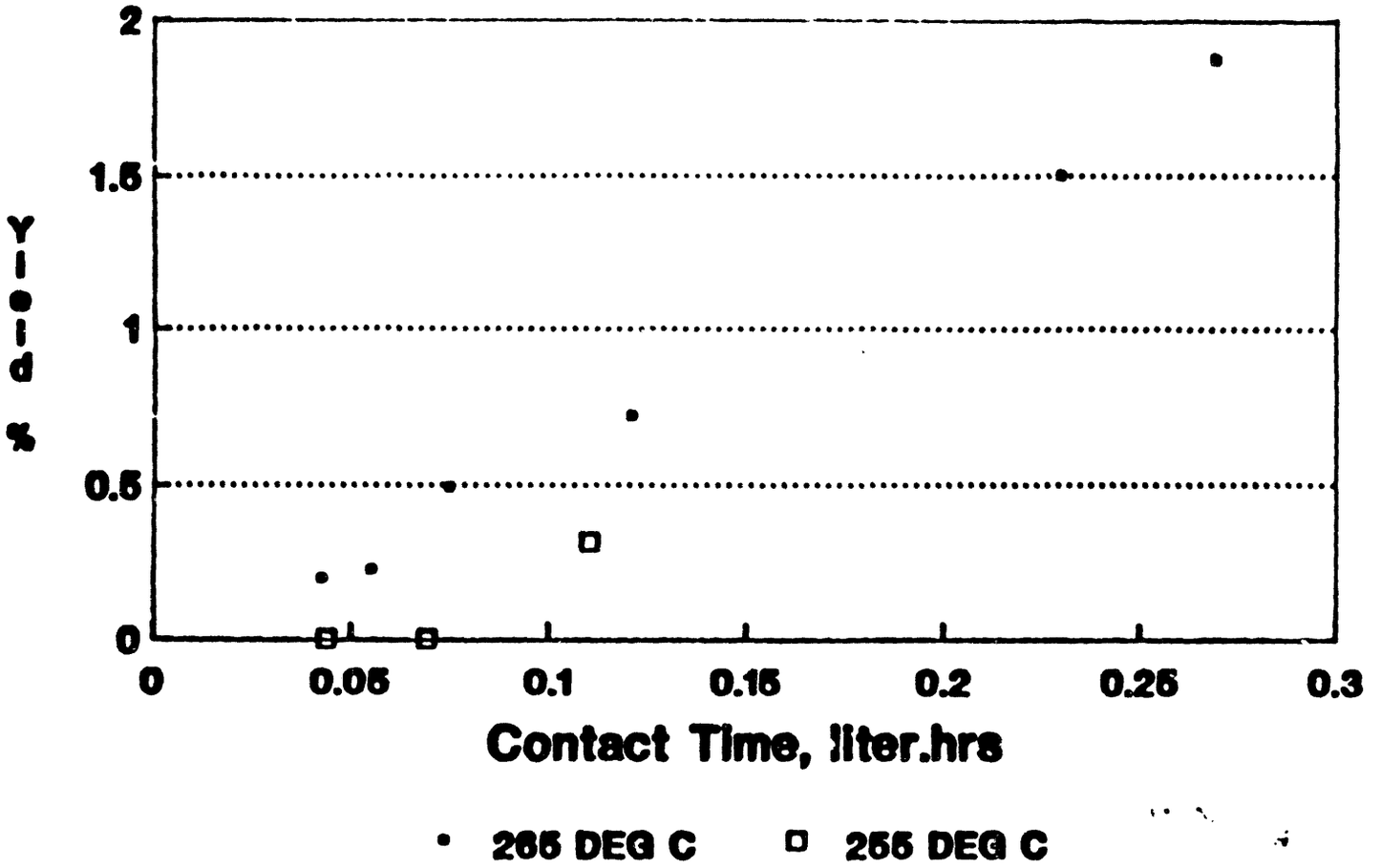


FIGURE A-42

Plant 700B, Run 43

Contact Time/Ethanol Yield

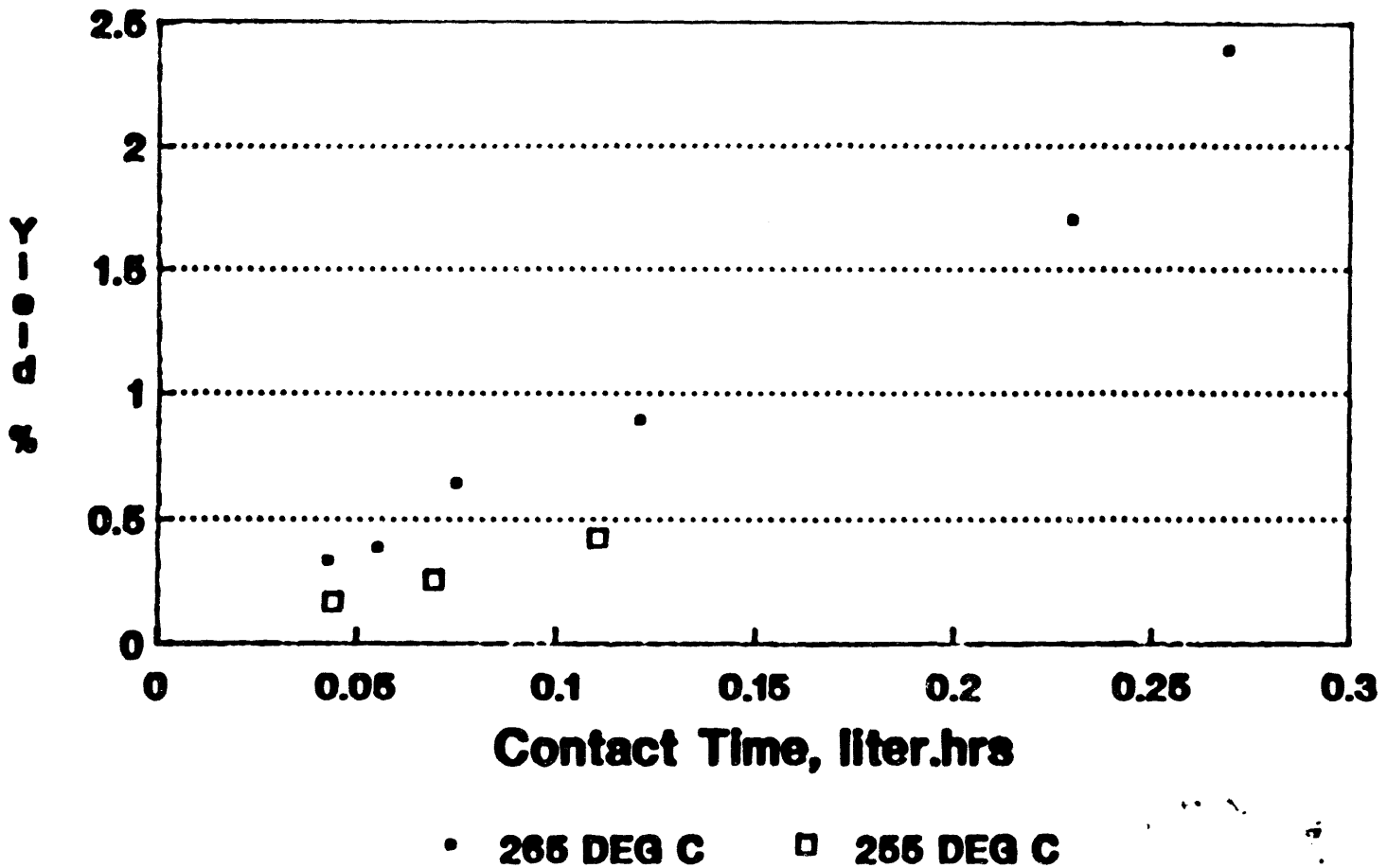


FIGURE A-43

Plant 700B, Run 43
Contact Time/Propene Yield

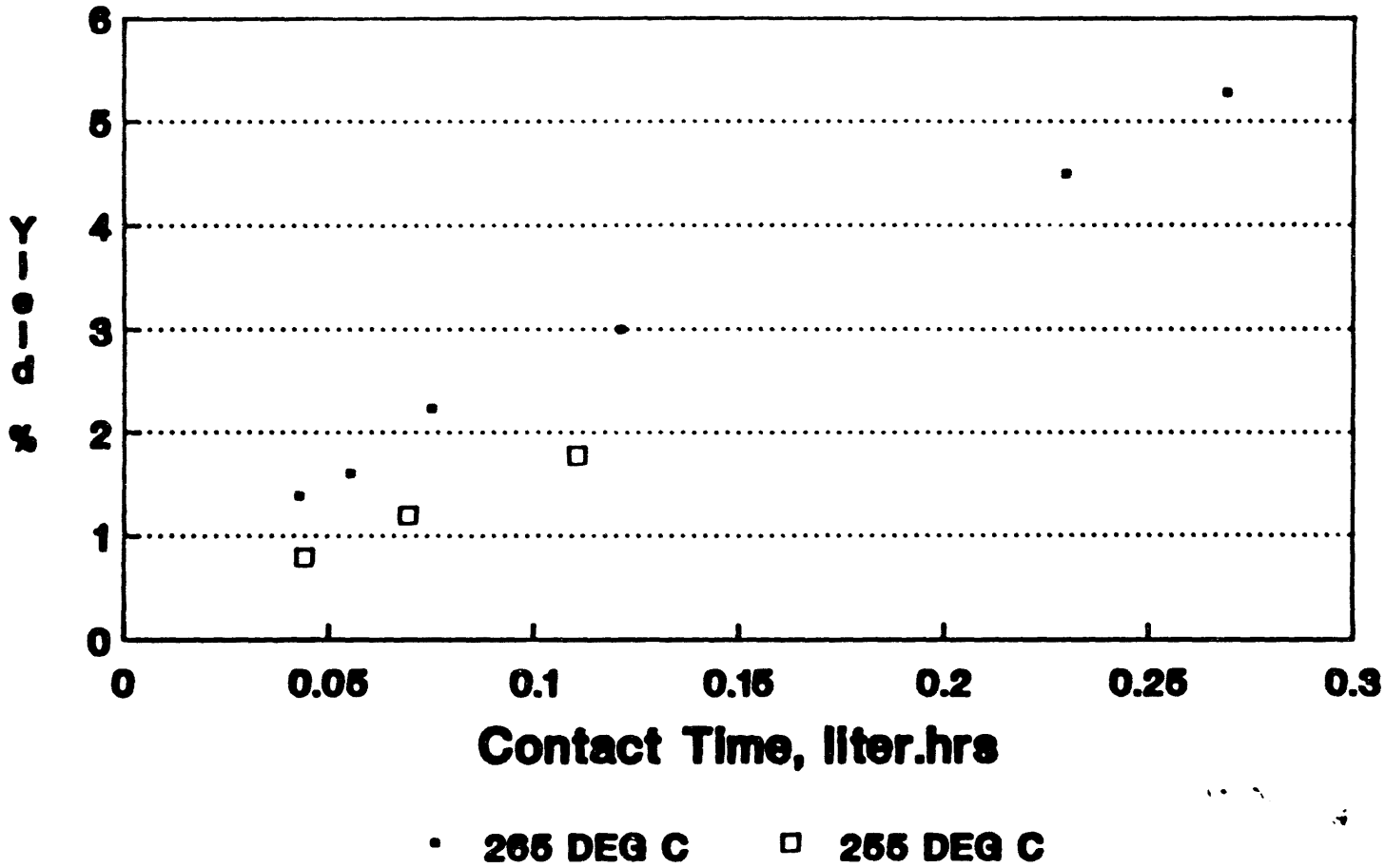


FIGURE A-44

Plant 700B, Run 43
Contact Time/Propane Yield

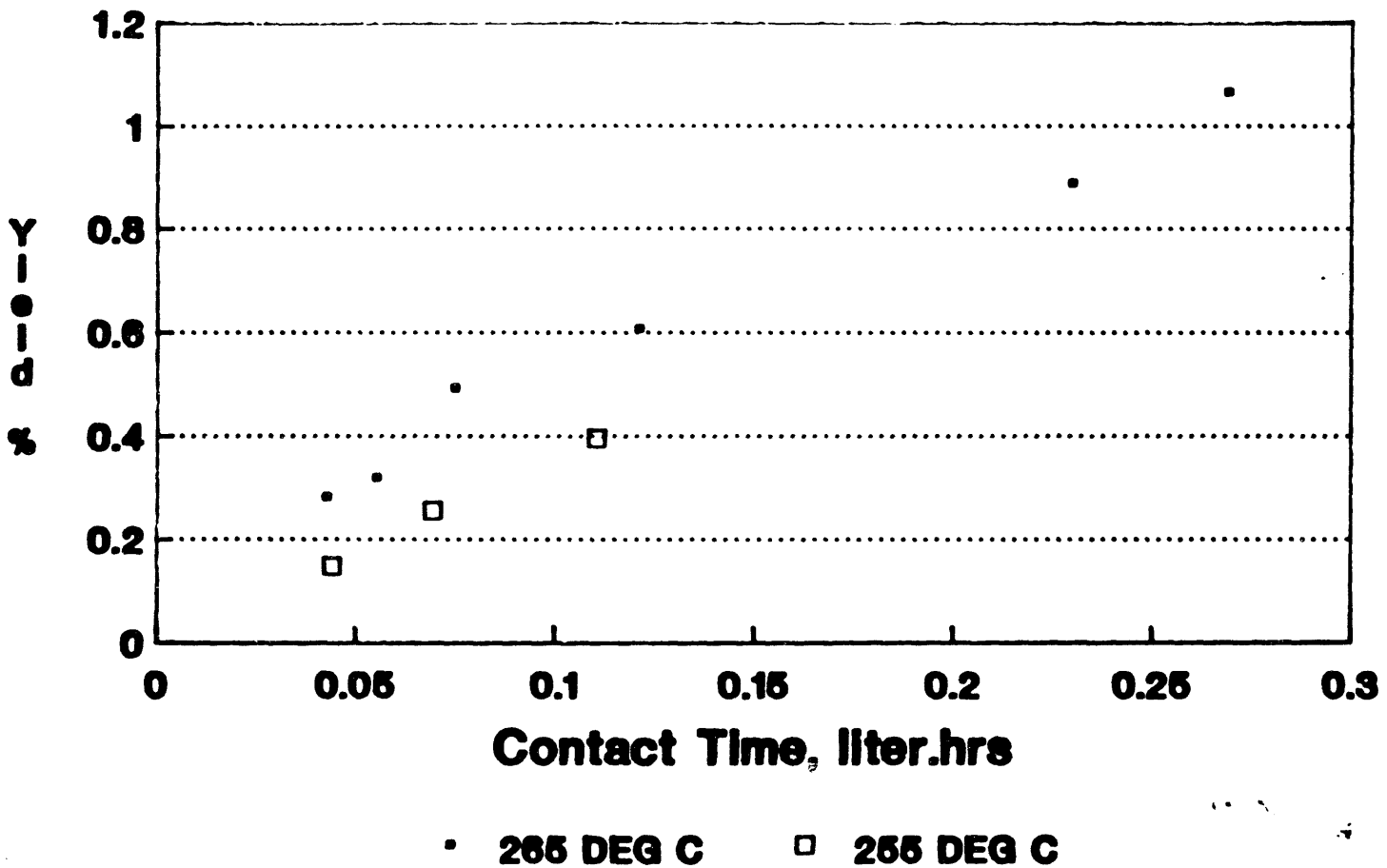


FIGURE A-45

Plant 700B, Run 43
Contact Time/Propanol Yield

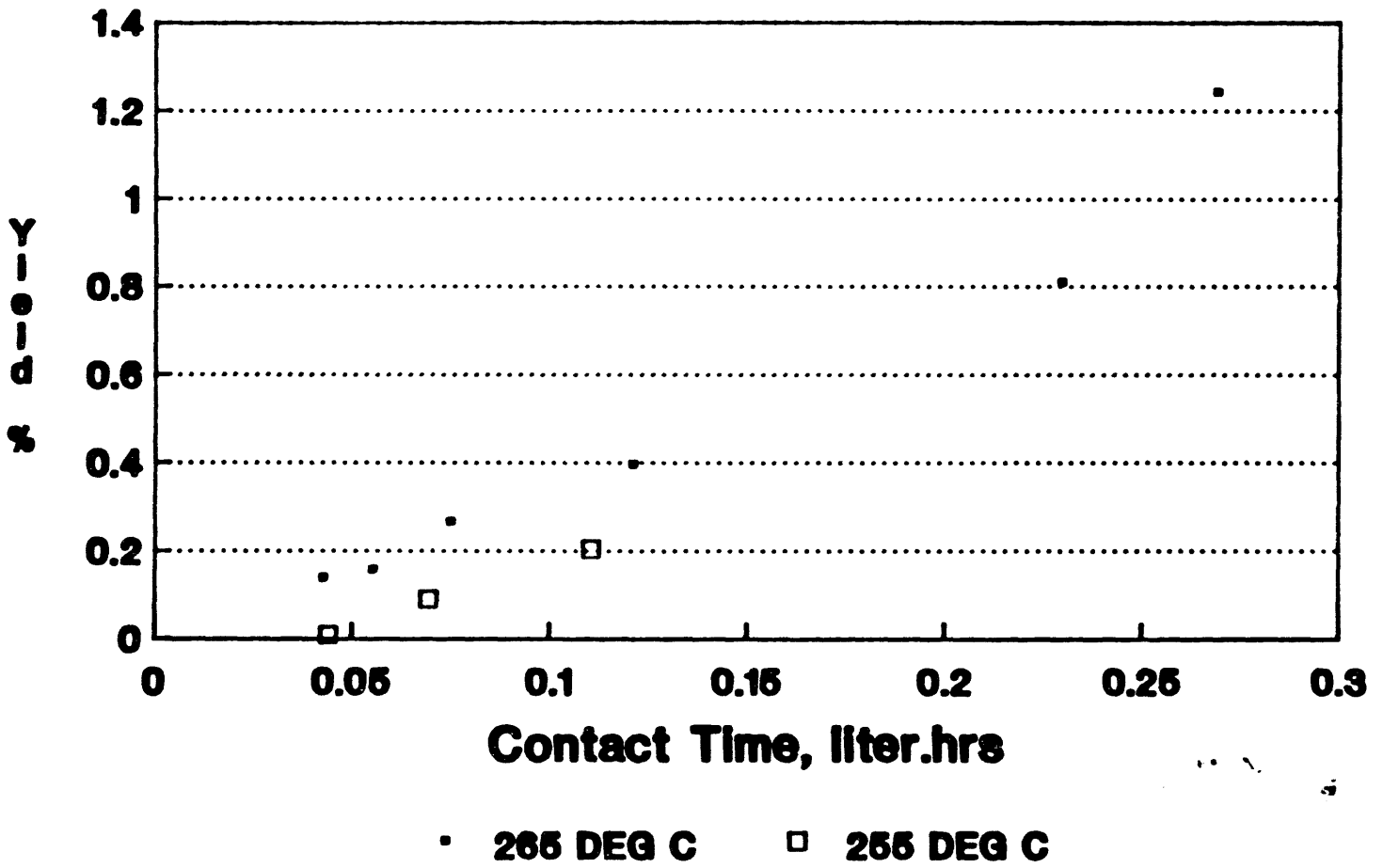


FIGURE A-46

Plant 700B, Run 43
Contact Time/Butene Yield

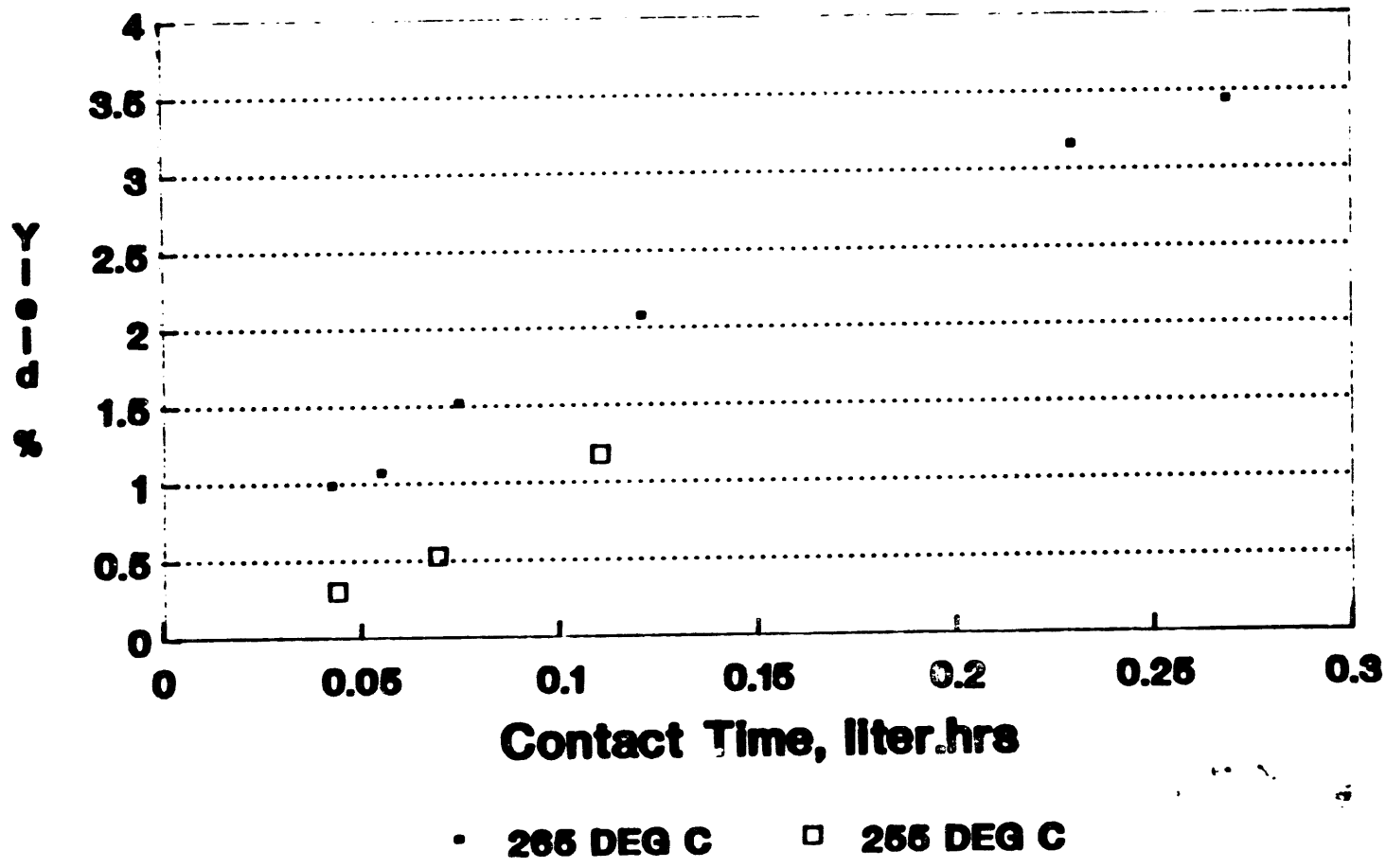


FIGURE A-47

Plant 700B, Run 43
Contact Time/Butane Yield

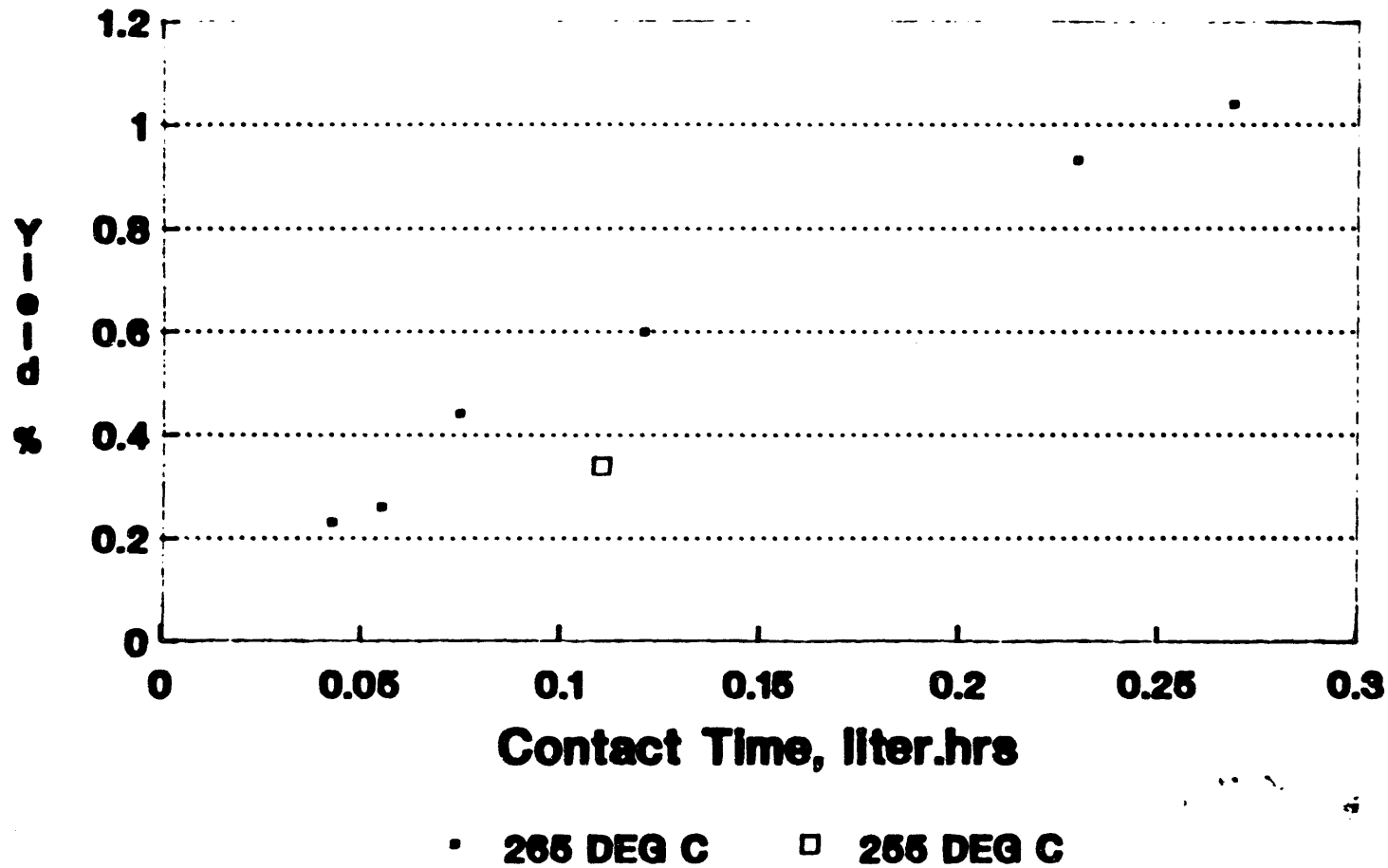
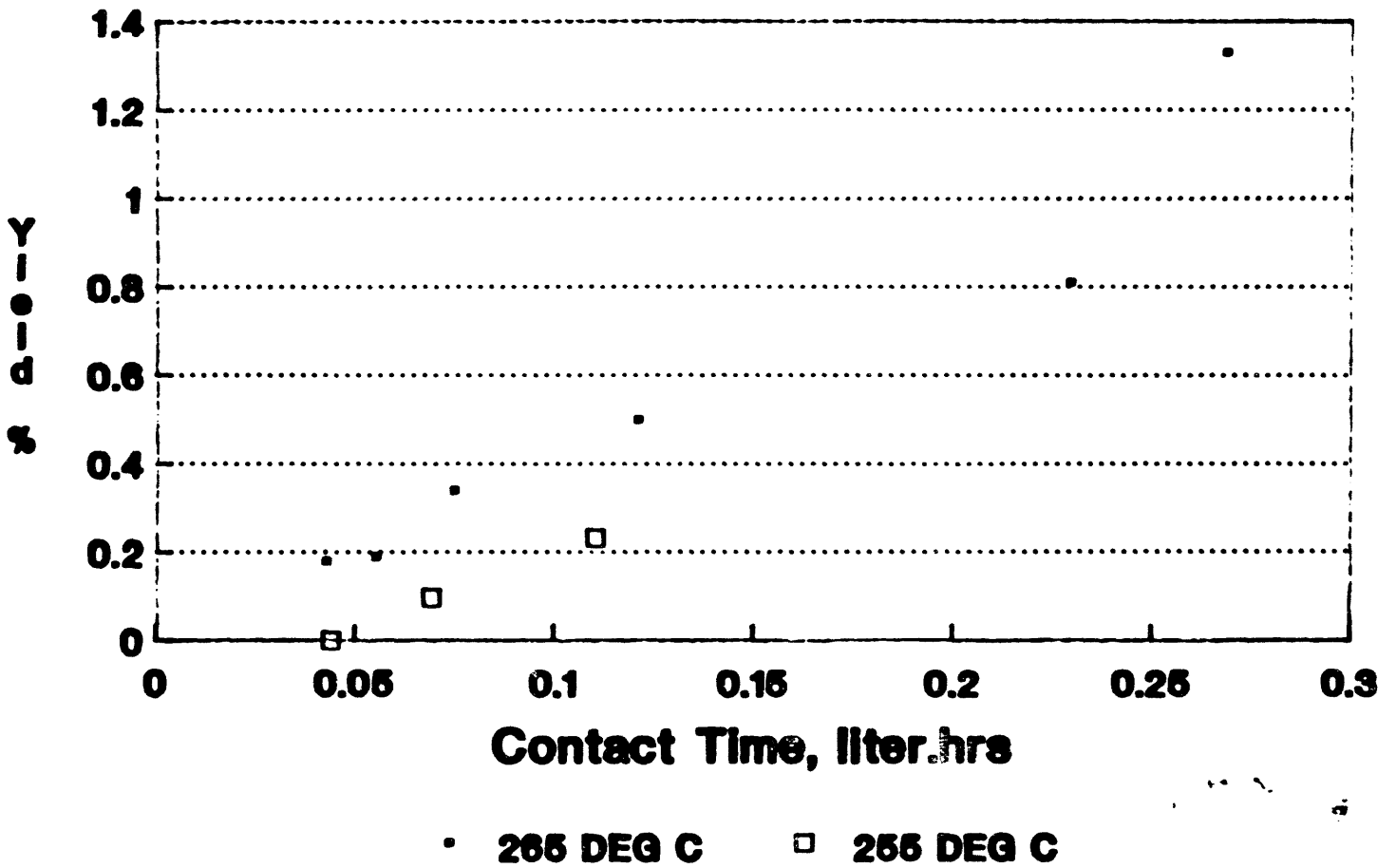


FIGURE A-48

Plant 700B, Run 43
Contact Time/Butanol Yield



DATE
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2/16/94

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