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DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

NOV 2 2 1993

Contract DE-AC22-89PC89869

by

Robert R. Frame and Hemant B. Gala

UOP
25 E. Algonquin Road
Des Plaines, Illinois

Technical Progress Report No. 12
(7/01/92-9/30/92)

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Contract Objective

The objective of this contract is to examine the relationship between catalytic properties and the function of cobalt Fischer-Tropsch catalysts and to apply this fundamental knowledge to the development of a stable cobalt-based catalyst with a low methane-plus-ethane selectivity for use in slurry reactors.

Contract Tasks

Task 1.0: Project Management Report

Task 2.0: Reference Cobalt Catalyst

Task 3.1: Modifier Role for Ruthenium

Task 3.2: Particle Size Effects with Ruthenium

Task 4.1: Identification of the Synergy between Cobalt and a Second Bimetallic Element, such as Ruthenium

Task 4.2: Development of a Bimetallic Catalyst

Task 5.0: Demonstration of Stability

Experimental

The fixed bed pilot plant, the catalyst testing procedure, and the calculations for conversion and selectivities were previously described in the technical progress report covering the period of 3/16/88 to 6/16/88 for Contract DE-AC22-87PC79812. Conversions and hydrocarbon selectivities were calculated using data from an on-line gas chromatography (GC) analyzer. Alcohol selectivities were calculated using data from an on-line boiling point GC analyzer which analyzed the liquid product.

The catalysts were prepared via the steps of impregnation, calcination, and reduction on a special Y-zeolite-derived support. The impregnation step consisted of evaporation of metal salts on to the support from an aqueous solution. For one catalyst (No. 6531-188) the metal salts were evaporated on to the support from a reverse micelle solution containing the metal salts. All the catalysts were calcined for four hours at 450°C. The calcined catalysts were loaded in the reactor with a diluent (usually quartz sand) and reduced in-situ for four hours in flowing hydrogen at 350°C. The diluent helps in the removal of heat from the very exothermic Fischer-Tropsch reaction. The catalyst preparation method is summarized in detail in Figure 1.

For all the runs discussed in this report, 13 g of powdery catalyst was loaded with 160 g of 60 to 80 mesh quartz sand (as diluent). All of the experimental catalysts were screened by a three condition screening test (Table 1) wherein the initial condition (least strenuous) was the same as used for the reference TC 211 catalyst (Run 65). The initial operating condition were chosen to allow for a direct performance comparison between the TC 211 catalyst and the experimental catalysts. When the experimental catalysts were found to be less active than the reference catalyst, the second and third set of test conditions were used to provide higher conversions so that selectivities could be compared to the reference catalyst at comparable conversions. For cobalt catalysts methane selectivity is often lower at higher conversion. A goal of the current work is to develop high activity catalysts which exhibit low methane selectivity.

For catalyst testing runs discussed in this report and not summarized previously in earlier reports, run summary plots of conversions and selectivities vs hours-on-stream are attached in Appendix A. Catalyst compositions are shown in Table 2 and summary performance data are shown in Tables 3 and 4.

Scope of Work During Reporting Period

Five new catalysts were prepared and screened during this reporting period. They were compared to a reference Co-based catalyst (TC 211) which was developed under a previous DOE contract No. DE-AC22-84PC70028. The reference catalyst was prepared on a special steamed and acid-washed Y-zeolite support. The five new catalysts were prepared on a commercial product which is a specially-prepared Y-zeolite. The commercial support is a steamed Y-zeolite that is washed, but not extensively, with nitric acid during its manufacture. Prior to use this support was further washed with nitric acid in the laboratory. A special solvent was used to impregnate metals on to the reference catalyst, whereas the five new catalysts were prepared by aqueous or reverse micelle impregnation of the metals.

The laboratory washes were all done with nitric acid, but with different concentrations of it and for different times. The purpose of acid washing is to remove debris from the zeolite structure which might have resulted from the steaming. Acid washing must be properly managed; if it is too strenuous the crystallinity remaining after steaming is destroyed and an amorphous silica results. A successful acid wash is one which provides a product with nearly the same surface area and pore volume (high crystallinity) as the steamed material.

None of the five new catalysts contained ruthenium, since it was the objective of this work to determine whether additional washing could give better supports. When the best support is found ruthenium will be added to the catalyst.

The specially-prepared Y-zeolite is characterized by pores that are from 50 to 100 Å in diameter. Such pores are large enough to support 50-100 Å cobalt crystallites, a size considered optimal for Fischer-Tropsch catalysis. The reverse micelle impregnation method developed by UOP controls particle size by a different mechanism. It might not be needed for steamed Y-zeolite supports; however, periodically reverse micelle-impregnated Y-zeolite supported catalysts will be prepared to see if benefits in performance do result.

In the previous quarterly report (No. 11) for this contract, performance data for catalysts (6531-166, 6531-167, 6531-175 and 6531-176) which were prepared on the commercial steamed and lightly acid-washed Y-zeolite were reported. These catalysts were less active and more selective to methane than the reference catalyst. Some of the data for Runs 80, 81, and 82 are reported in Tables 2, 3, and 4. The current work was done to determine whether catalysts more similar to the reference catalyst would result if the light acid wash was supplemented by a laboratory acid wash.

Results and Discussion

Run 83

The catalyst used in this run, No. 6531-178, was supported on commercial steamed Y-zeolite which had been laboratory washed for 36 hours with 2M nitric acid (Table 2). This support contained 4.86 wt% aluminum compared to 5.24 wt% aluminum on the commercial steamed material before laboratory wash. The catalysts for this run and Run 80 (Catalyst No. 6531-176) were similar; they contained cobalt in nearly the same amount. The difference between the two catalysts was that the support for catalyst 6531-176 (Run 80) was not further washed in the laboratory.

The performance characteristics of the two catalysts were similar (Tables 3 and 4). The conversions were very close at all three conditions, as were the hydrocarbon and alcohol selectivities. Performance data from Run 83 as a function of hours-on-stream are shown in Figures A-1 to A-7.

Run 84

The catalyst used in this run, No. 6531-180 contained cobalt, manganese, and zirconium (Table 2). It was prepared on the same support that was used for catalyst 6531-178 (Run 83). The composition of this catalyst was comparable to catalysts 6531-166 (Run 82) and 6531-167 (Run 81). There was little difference in performance among the catalysts of Runs 81, 82, and 84 (Tables 3 and 4). Performance data from Run 84 as a function of hours-on-stream are shown in Figures A-8 to A-14.

Run 85

The catalyst used for this run, No. 6531-182 is the only one prepared on the 3.86 wt% aluminum support (Table 2). It was more active than the two catalysts, No. 6531-178 and 6531-180 prepared on the 4.83 wt% aluminum support (Table 3). The methane selectivity was lower and it represents an improvement over the two catalysts on the higher aluminum support. Rather than make more catalysts from the 3.86 wt% aluminum support, another, lower aluminum, support was prepared. Performance data from Run 85 are presented in Figures A-15 to A-21 as a function of hours-on-stream.

Run 86

This run used the first of two catalysts prepared on the most extensively washed of the supports (Table 2) described in this report. Furthermore, the catalyst, No. 6531-188 was the only one prepared by the reverse micelle impregnation route. As summarized in Tables 3 and 4, the catalyst activity was comparable to that of catalysts 6531-176 (Run 80) and 6531-166 (Run 82) and lower than that of catalyst 6531-182 (Run 85). Performance data from Run 86 are shown in Figures A-22 to A-28.

Run 87

The second of the two catalysts prepared on the most extensively washed supports was evaluated in this run. This catalyst (No. 6531-186) was prepared by aqueous impregnation. It exhibited superior activity to all the others catalysts discussed in this report(Table 3). The initial conversion was even better than the reference TC 211 catalyst. The methane selectivity just after startup at Condition 1 was low compared to the other four in this report but still greater than the selectivity observed for the reference catalyst (Run 65). The high initial activity was decreasing throughout the time at the initial condition. Incorporation of metal additives would be expected to forestall this activity loss and decrease methane selectivity. The important observation during this run was that the most extensively acid-washed support was better than the earlier, less extensively acid-washed supports. Because of the promise shown by the catalyst the run was extended in order to evaluate its performance a second time at condition 1. This last part of the run confirmed that activity loss had occurred during the run, and that stabilization of the catalyst is required.

Summary and Implications for Further Work

Additional work was done with the commercially steamed/acid-washed Y-zeolite support described in the Technical Progress Report No. 11. The catalysts described in that report were prepared from the commercial steamed Y zeolite as received. In the current work the commercial material was further acid washed and then used for impregnation of the metals.

The commercial steamed Y-zeolite contained 5.24 wt% aluminum. The laboratory washes were with various concentrations of nitric acid for various times. As the severity of the laboratory acid wash increased, the percent aluminum remaining decreased. In spite of the aluminum loss the crystallinity of the support was apparently maintained because the high surface area of the pre-laboratory washed sample was retained. The steaming creates amorphous material which is at least in part alumina. When acid washing is properly done this amorphous material is removed and pores that might have been blocked are re-opened.

In the future even more extensively washed supports will be prepared from the commercial steamed Y zeolite. Use of additional metals such as manganese and zirconium will be investigated as a way to improve the performance of the catalysts on the better supports such as the one used for the catalyst of Run 87. Stability and methane selectivity improvements are particularly desired. Furthermore, the special impregnation solvent used in the earlier work leading to the reference catalyst will also be evaluated. Finally, ruthenium will be incorporated in the better catalysts to enhance activity.

Table 1
Operating Conditions for the Three Condition Test

Key Variables	Condition 1	Condition 2	Condition 3
Pressure, psig	287	287	287
Temperature, °C	211	231	231
Feed rate, (NL/hr/g Co)	4.9	4.9	2.5

Table 2
Catalyst Properties

Support Properties				Catalyst No.	Run No.	Catalyst Metals by AAS, wt-%		
Treatment	SA[1]	PV[2]	Al[3]			Co	Mn	Zr
Steamed	591	0.51	5.24	6531-176 6531-167 6531-166	80 81 82	7.5 8.1 7.3	0.4 0.6	1.0 1.0
Steamed/ HNO_3[4]	562	0.49	4.83	6531-178 6531-180	83 84	7.7 8.5	1.7	1.1
Steamed/ HNO_3[5]	586	0.51	3.86	6531-182	85	9.4		
Steamed/ HNO_3[6]	596	0.54	2.94	6531-188 6531-186	86 87	9.1 8.9		

[1] m^2/g
[2] cc/g
[3] wt-%
[4] Wash 36 Hours with 2M HNO_3
[5] Wash 36 Hours with 3M HNO_3
[6] Wash 72 Hours with 3M HNO_3

Table 3
Activity and Hydrocarbon Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Hydrocarbon Selectivity, %				
			C_1	C_2	$C_2^=$	C_3	$C_3^=$
65	1	58	7	0.6	0	1.7	2.0
80	1	41	18	1.8	0	2.8	1.9
	2	77	18	1.8	0	2.9	1.2
	3	86	17	2.2	0	3.0	1.1
83	1	43	18	2.5	0	3.2	2.4
	2	70	20	2.5	0	3.2	2.0
	3	81	20	2.5	0.1	3.2	1.7
81	1	35	18	3.2	0	4.0	3.0
	2	78	17	2.8	0.2	3.5	2.2
	3	82	18	3.0	0.2	3.7	2.3
82	1	40	17	3.8	0	6.0	4.0
	2	75	18	3.3	0.2	5.0	2.1
	3	85	17	3.0	0.2	5.0	1.5
84	1	32	18	4.1	0	5.1	4.1
	2	72	16	3.6	0.2	4.2	3.0
	3	85	17	3.3	0.2	3.8	2.7

[redacted] [redacted]

Table 3 (Continued)
Activity and Hydrocarbon Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Hydrocarbon Selectivity, %				
			C_1	C_2	$C_2^=$	C_3	$C_3^=$
65	1	58	7	0.6	0	1.7	2.0
85	1	51	15	1.6	0	2.1	2.0
	2	83	14	1.6	0	2.1	1.5
	3	95	13	1.7	0	2.4	1.3
86	1	40	15	3.2	0	4.2	5.0
	2	82	15	3.0	0	4.0	3.0
	3	85	16	3.0	0	3.1	3.0
87	1	82	10	1.1	0.1	1.3	2.0
	2	90	13	1.3	0	2.0	1.0
	3	95	12	1.4	0	2.0	1.1

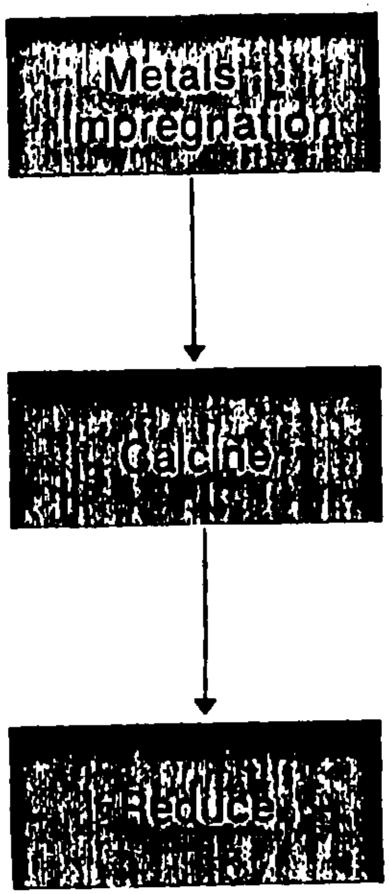
Table 4
Activity and Alcohol Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Alcohol Selectivity, %		
			C_2	C_3	C_4
65	1	58	0.5	0.6	2.0
80	1	41	0.1	0	0
	2	77	0.1	0.03	0.01
	3	86	0.1	0.02	0.01
83	1	43	0.3	0	0
	2	70	0.2	0.03	0.01
	3	81	0.2	0.03	0.01
81	1	35	0	0	0
	2	70	0.2	0.05	0.02
	3	82	0.1	0.02	0.02
82	1	40	0.4	0.1	0
	2	75	0.2	0.05	0.03
	3	85	0.1	0.03	0.02
84	1	32	0.4	0.1	0.08
	2	72	0.3	0.1	0.05
	3	85	0.2	0.08	0.03

Table 4 (Continued)
Activity and Alcohol Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Alcohol Selectivity, %		
			C_2	C_3	C_4
65	1	58	0.5	0.6	2.0
85	1	51	0.3	0.2	0.1
	2	83	0.1	0.05	0.05
	3	95	0.1	0.05	0.05
86	1	40	0.5	0.2	0.15
	2	82	0.4	0.2	0.1
	3	85	0.2	0.1	0.05
87	1	82	0.2	0.05	0.03
	2	90	0.4	0.1	0.03
	3	95	0.2	0.03	0

Figure 1
Standard Catalyst Preparation



Aqueous or special solvent

Rotary Evaporation at 100°C

450°C, Hold 4 hours

350°C, H2, 2 hours

APPENDIX A

CATALYST PERFORMANCE DATA
RUN SUMMARY

FIGURE A-1
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

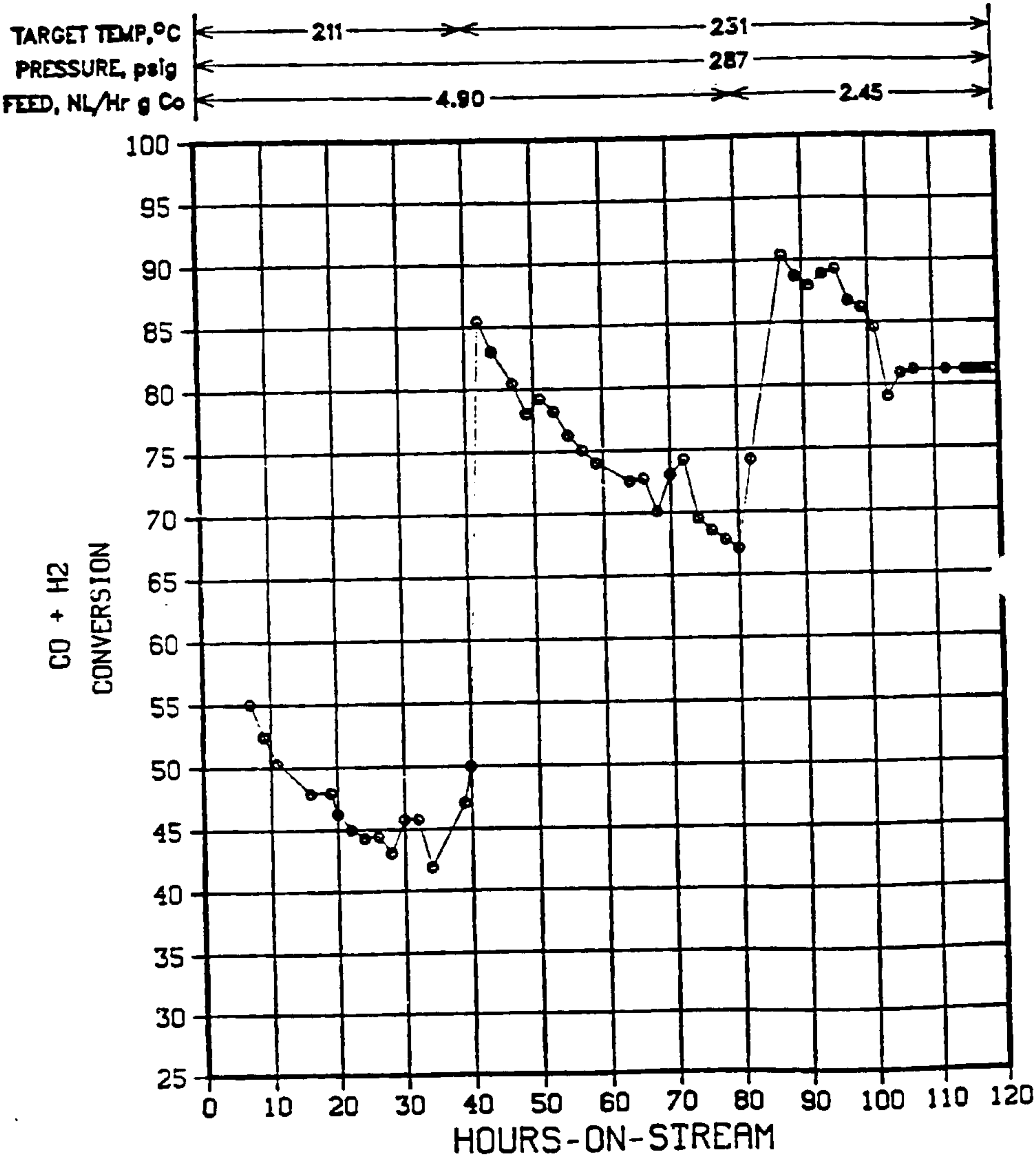


FIGURE A-2
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

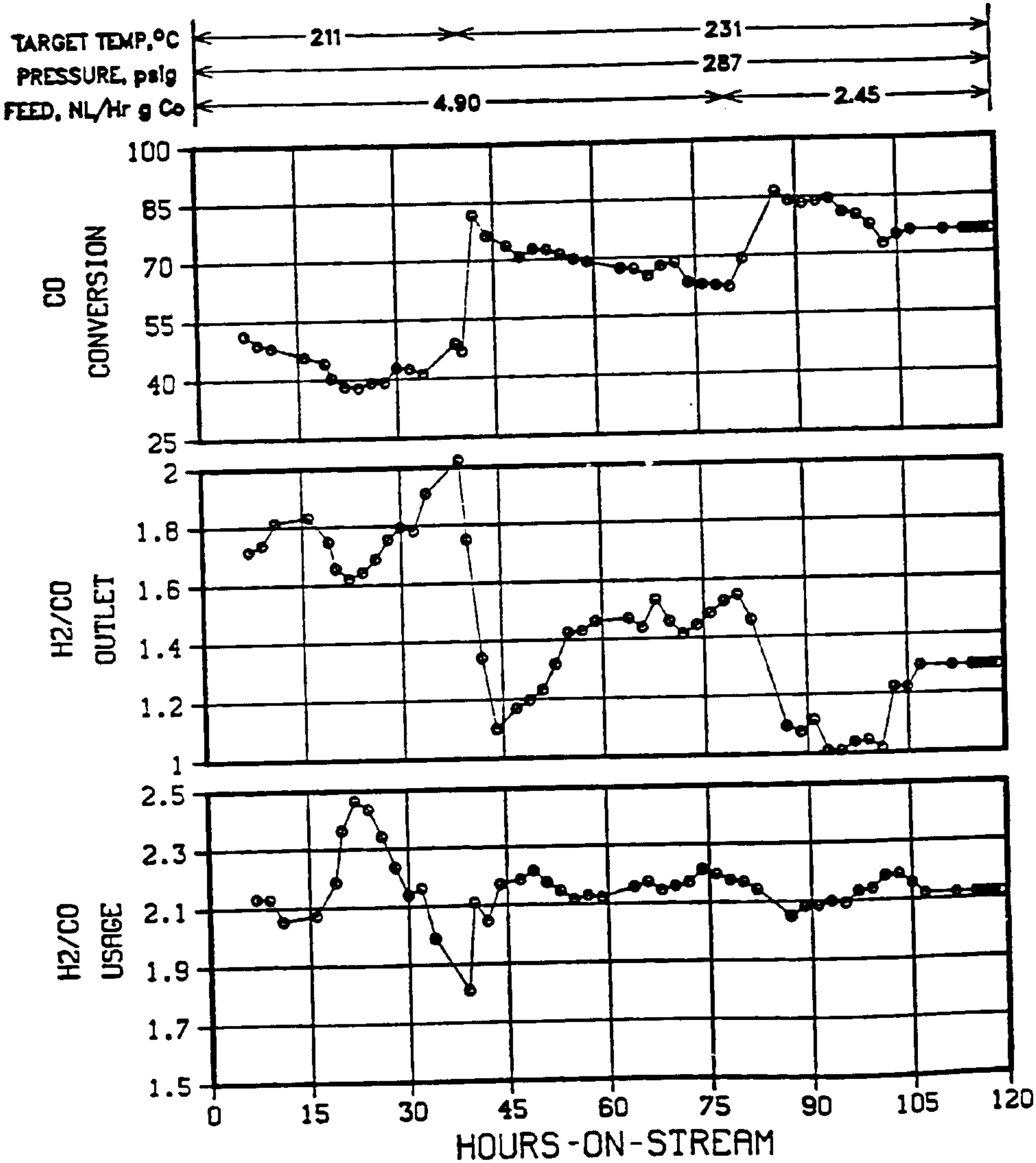


FIGURE A-3
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

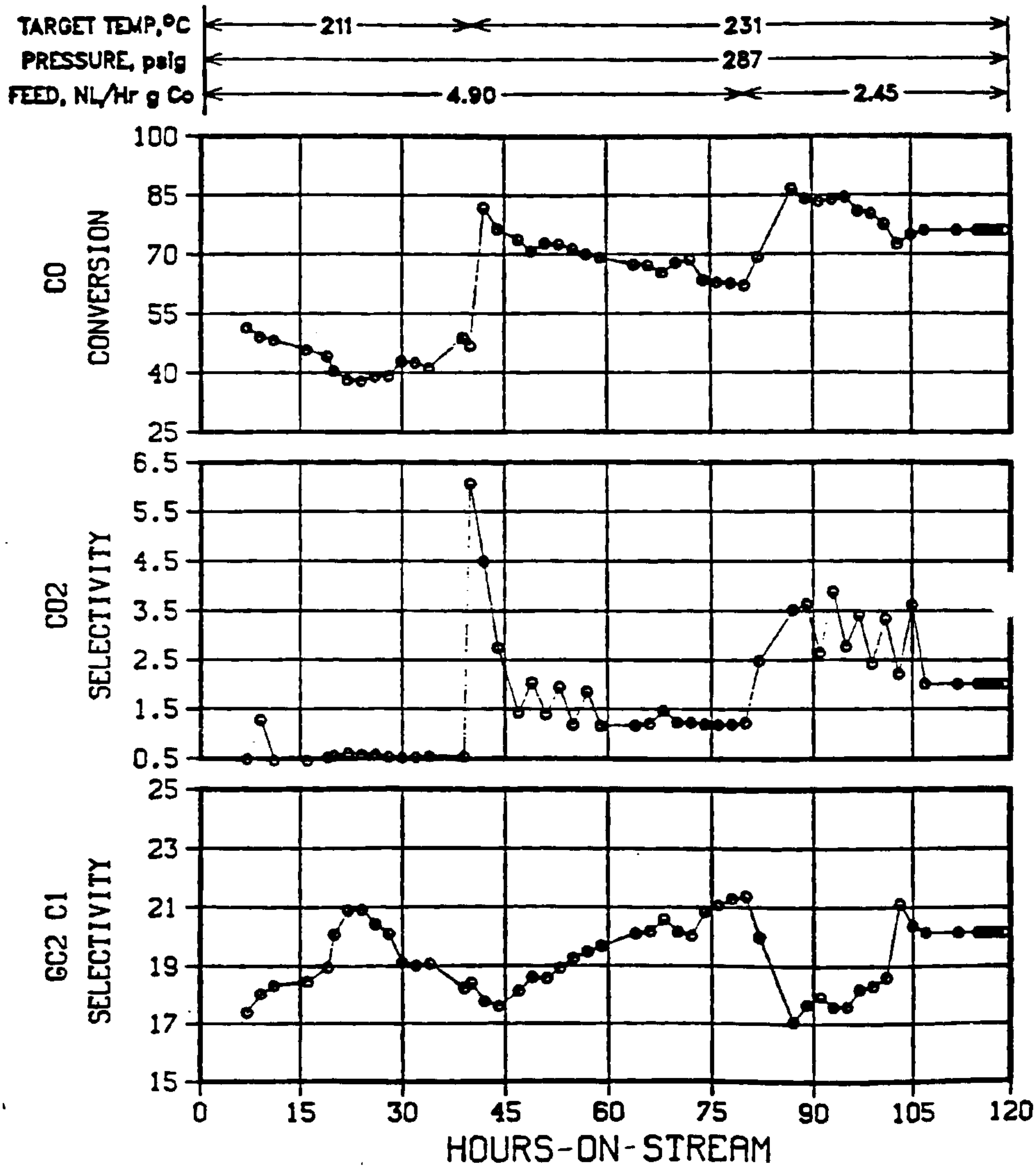


FIGURE A-4
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

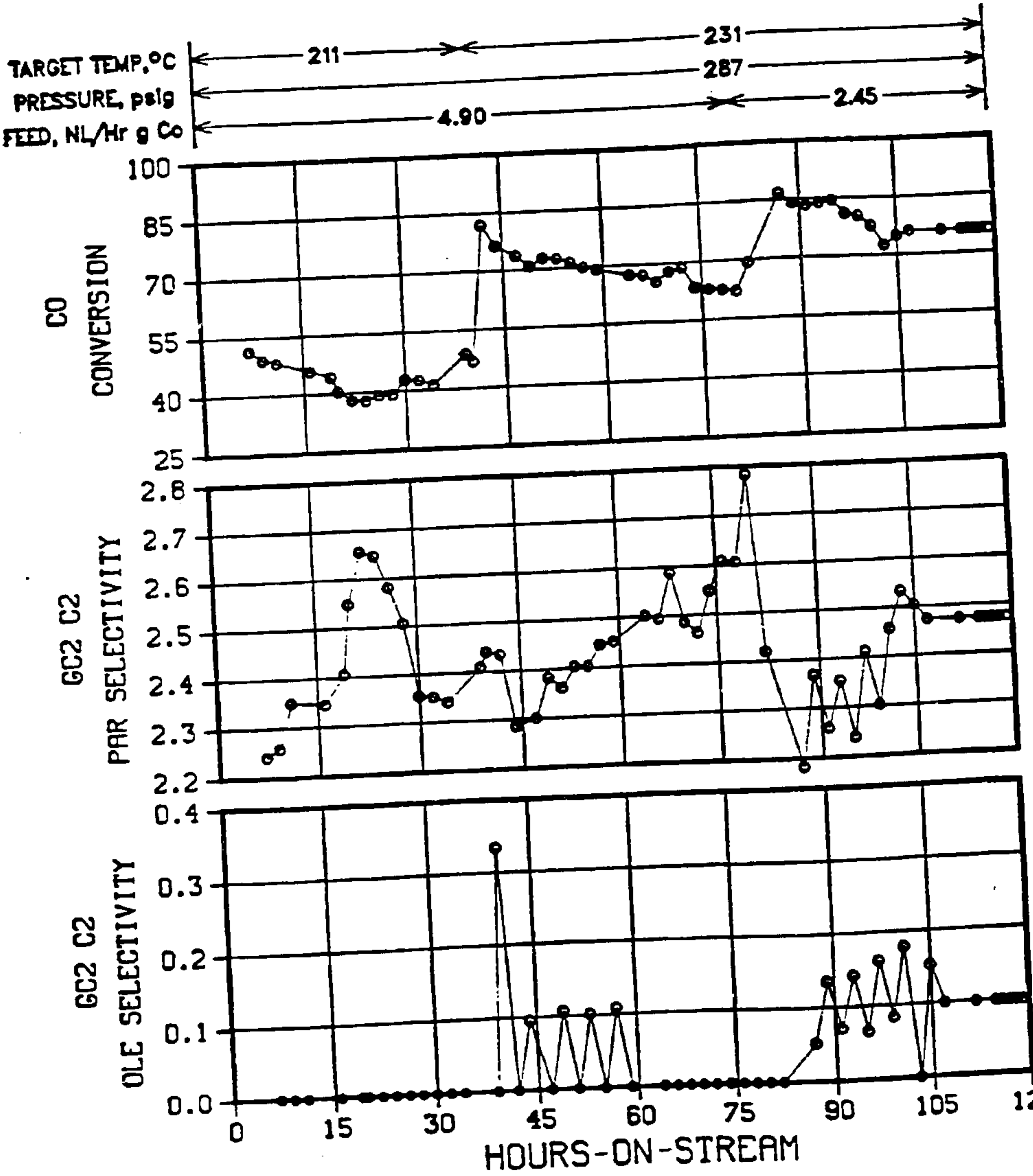


FIGURE A-5
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

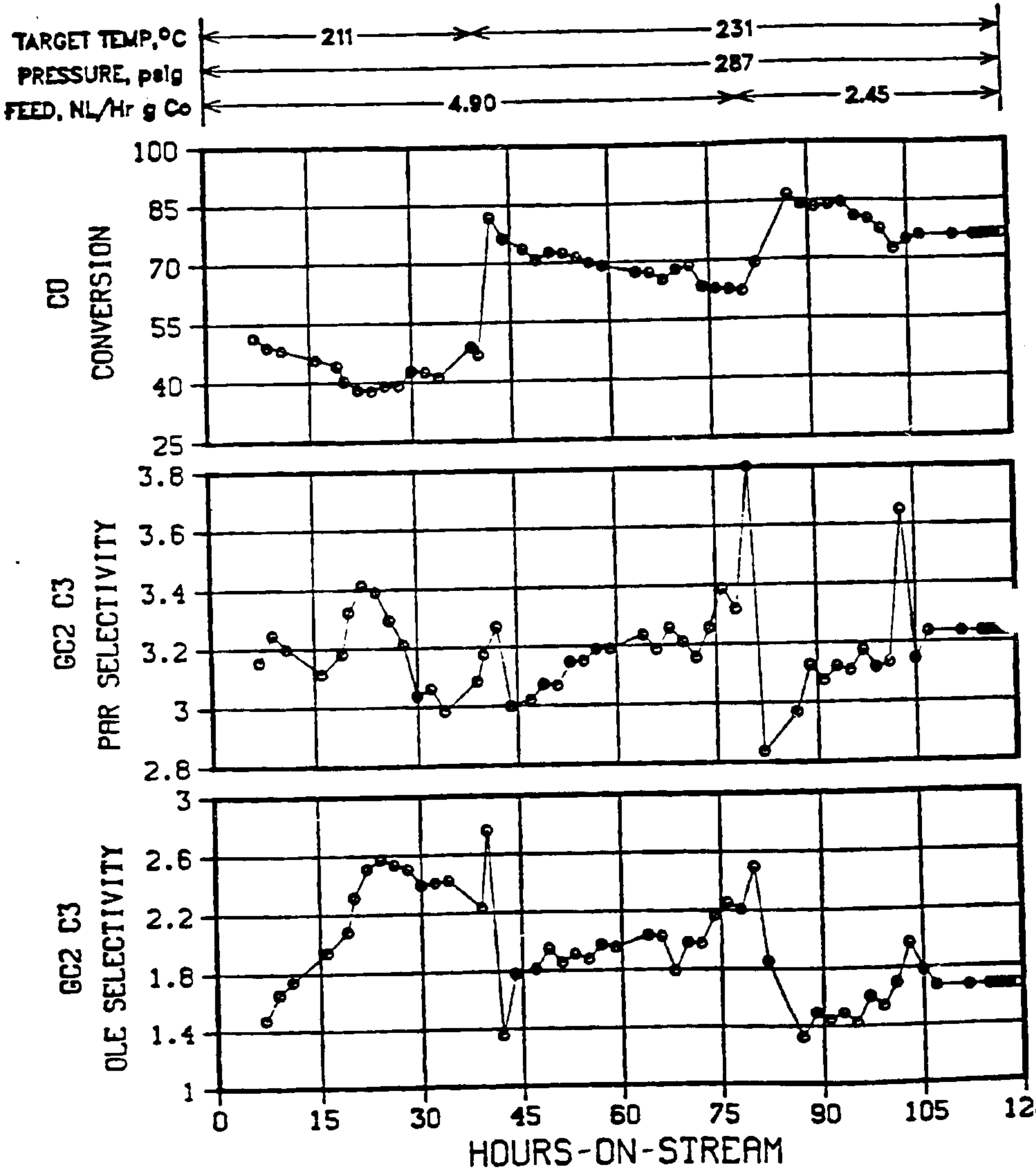


FIGURE A-6
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

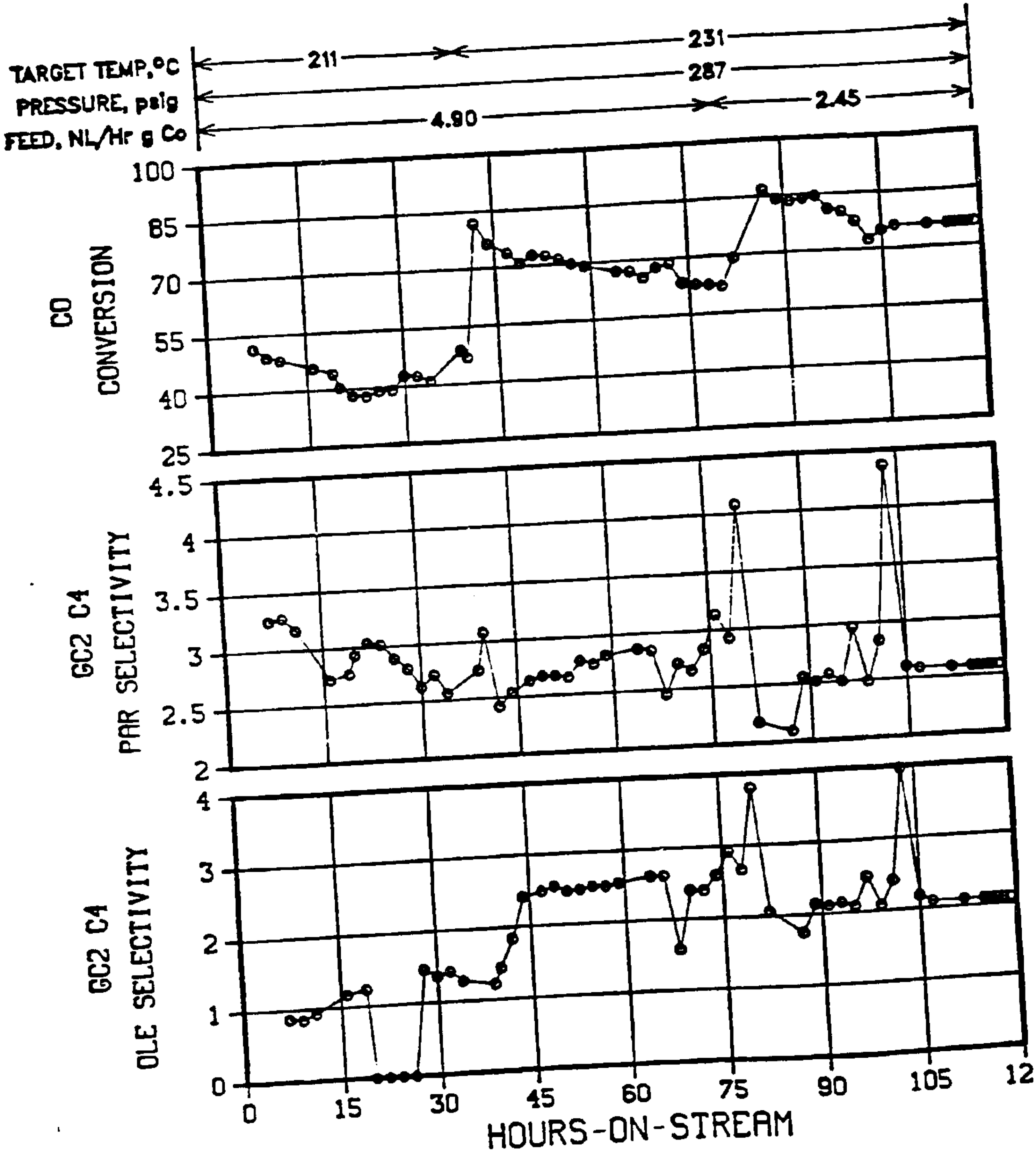


FIGURE A-7
SUMMARY DATA FOR RUN 83 (CATALYST 6531-178)

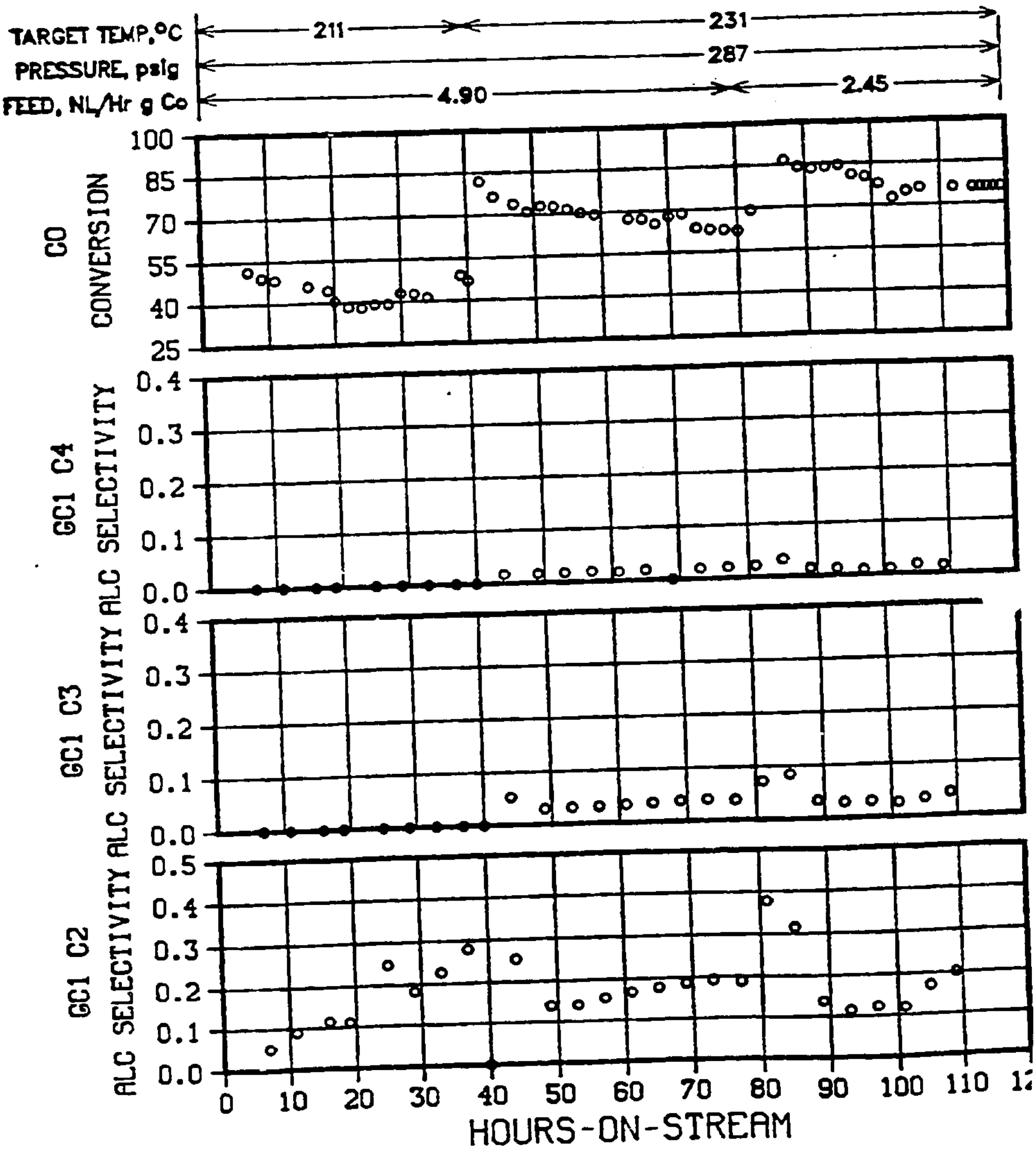


FIGURE A-8
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

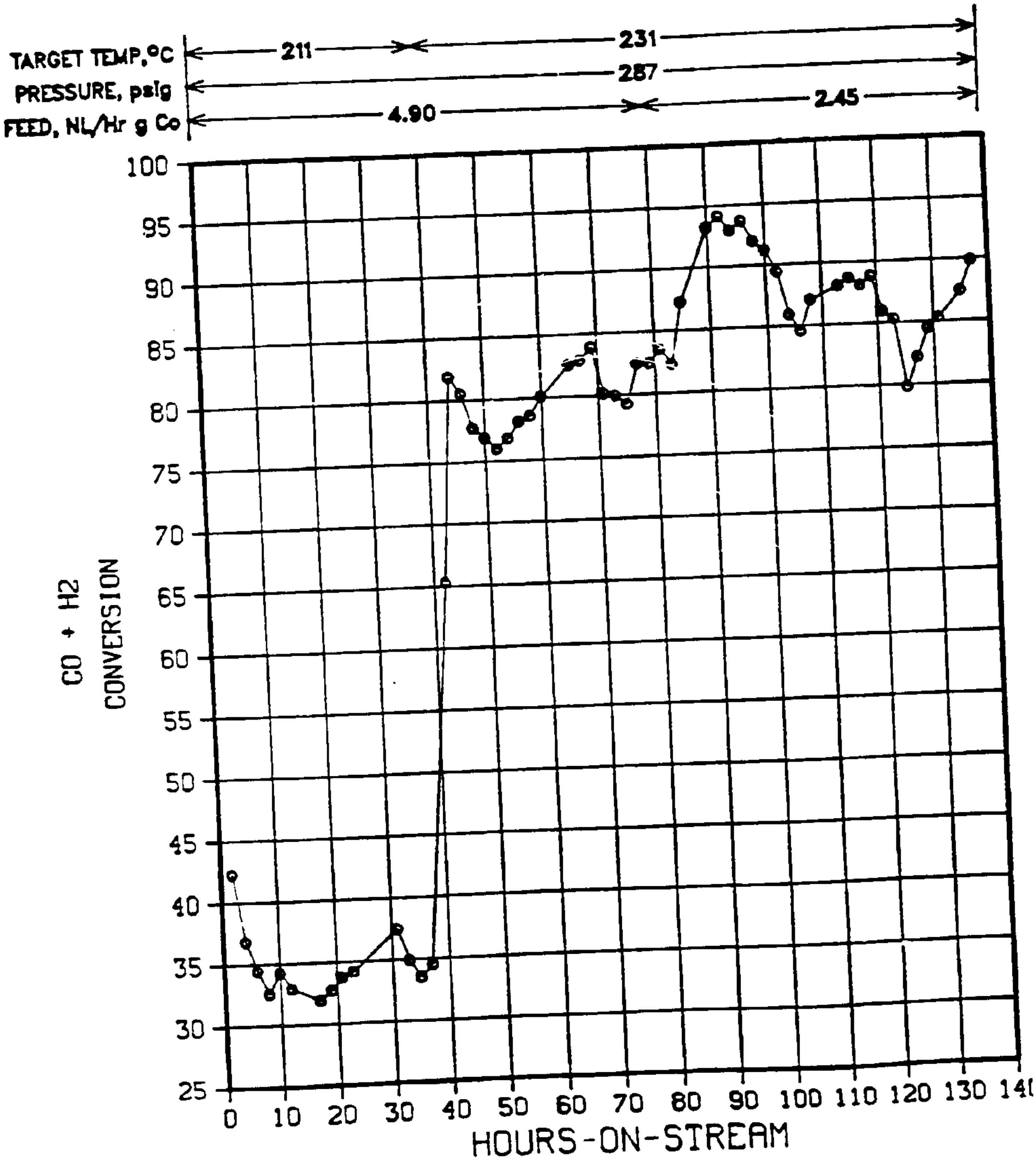


FIGURE A-9
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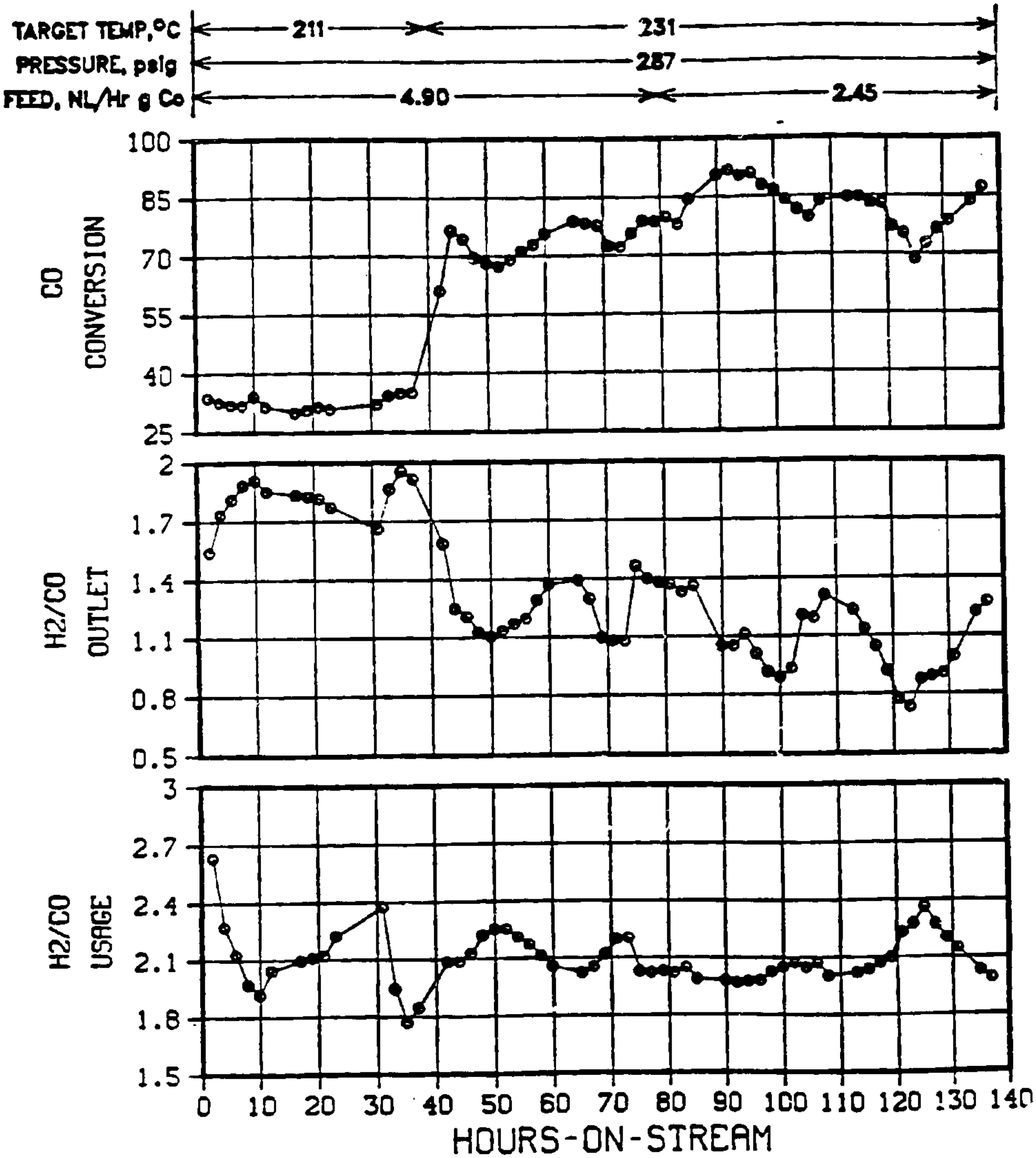

FIGURE A-10
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

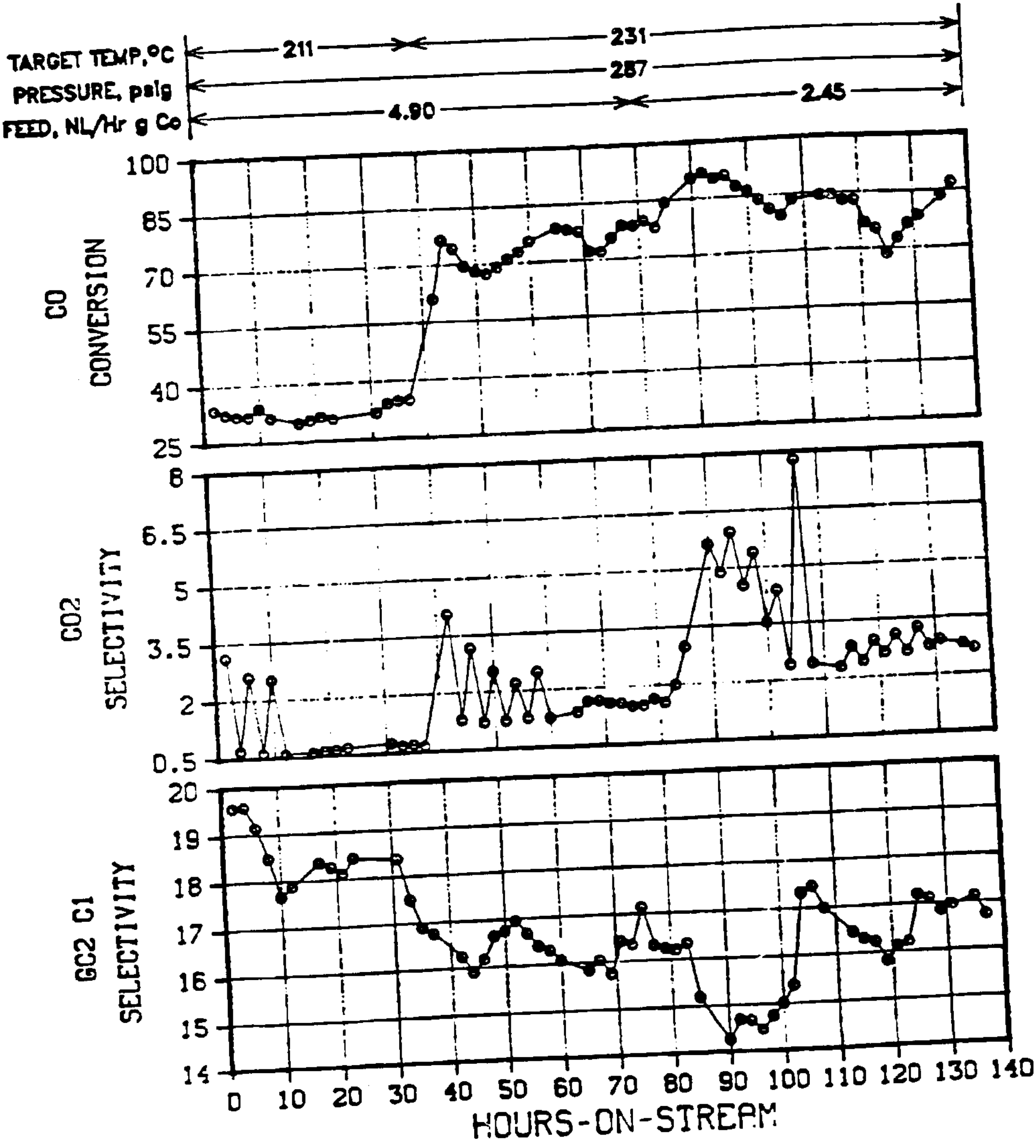

FIGURE A-11
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

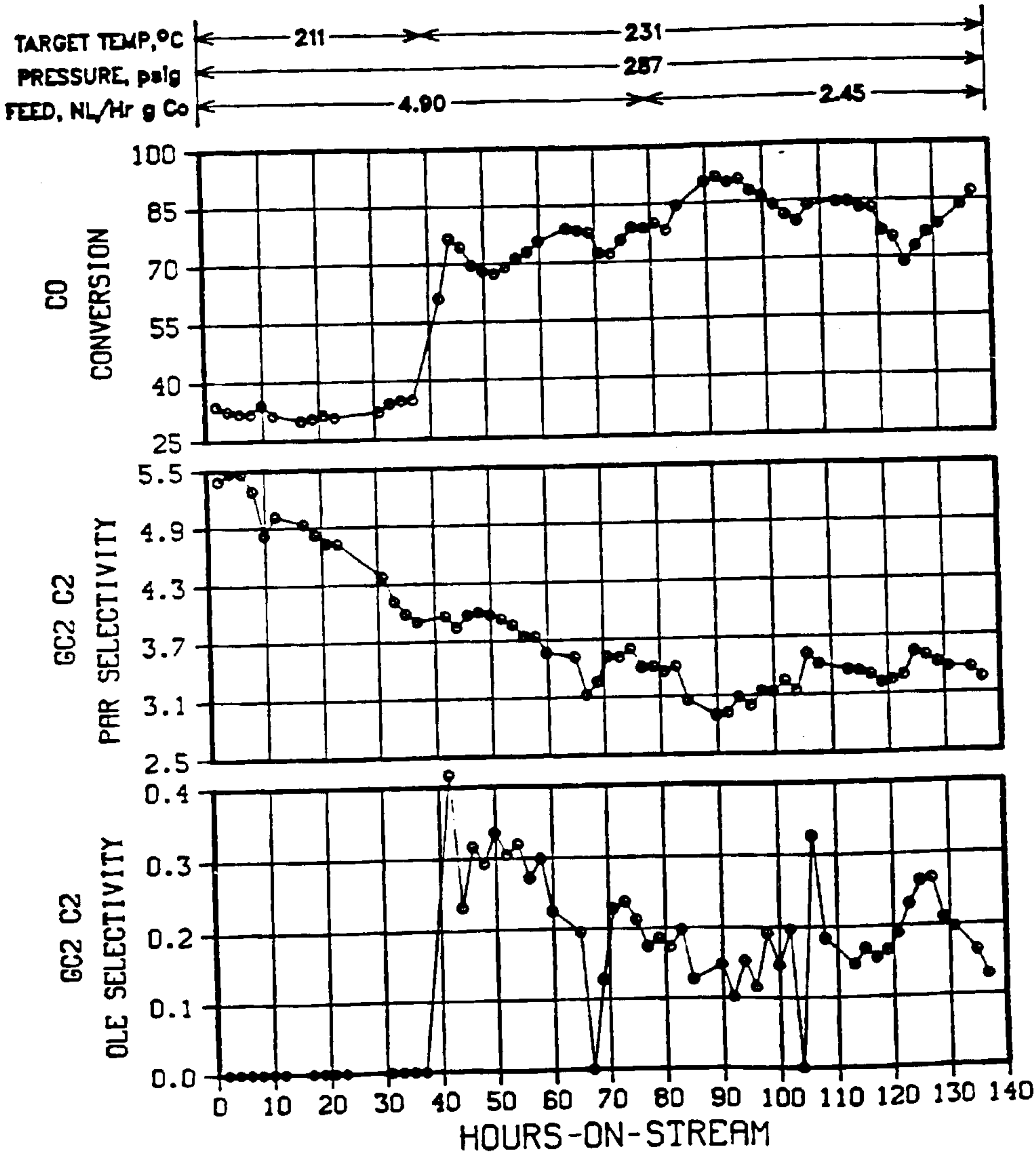

FIGURE A-12
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

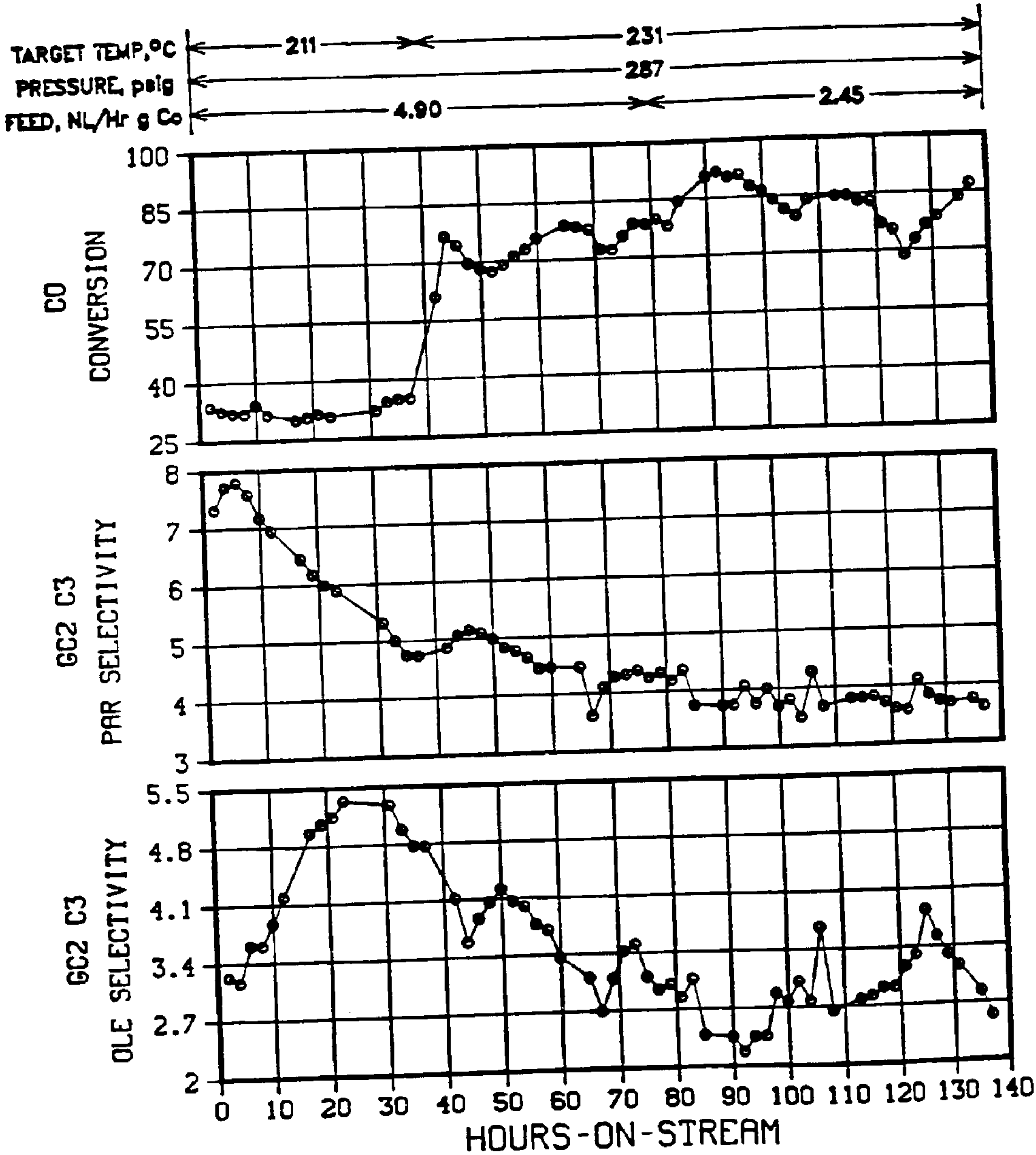

FIGURE A-13
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

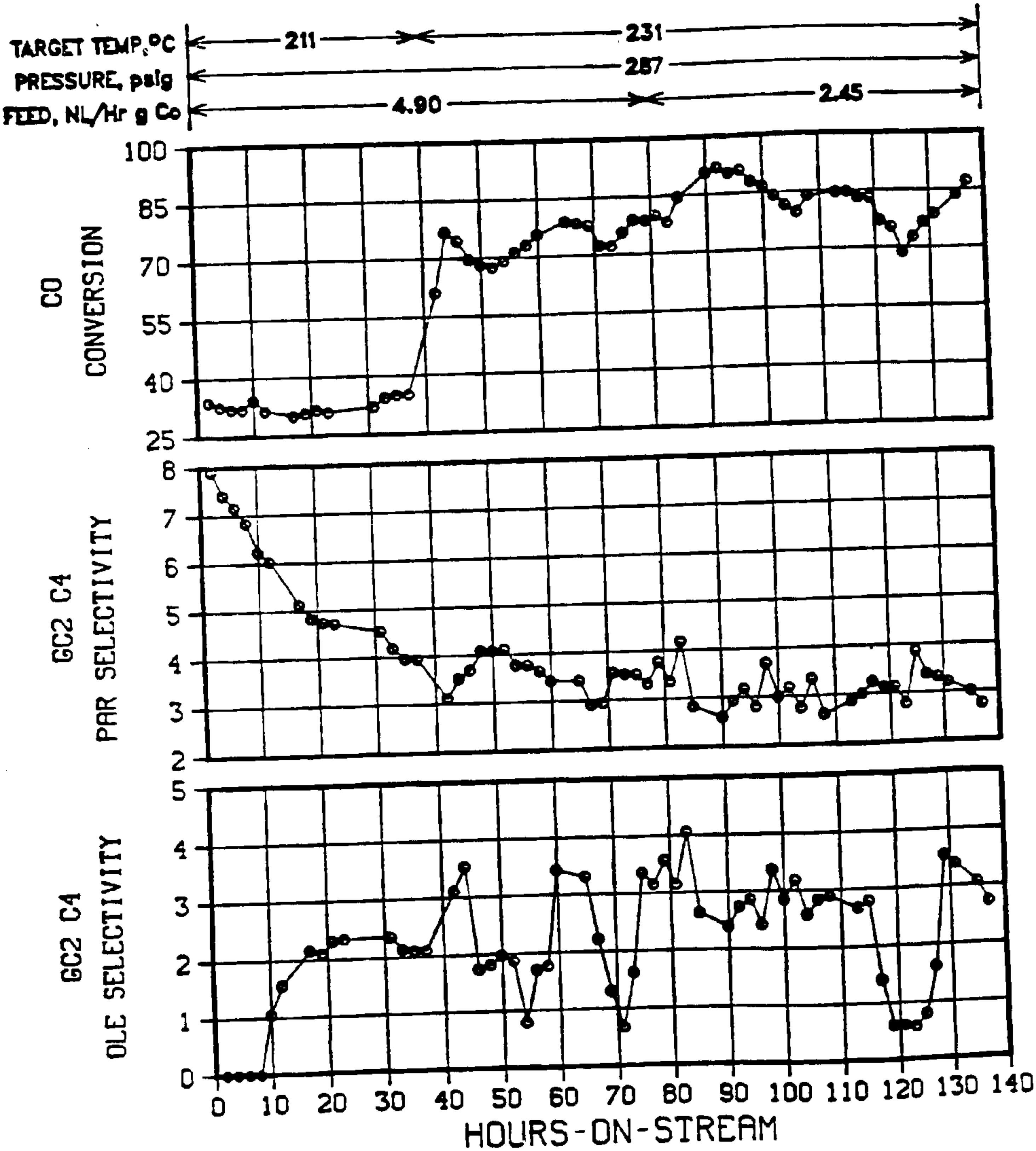

FIGURE A-14
SUMMARY DATA FOR RUN 84 (CATALYST 6531-180)

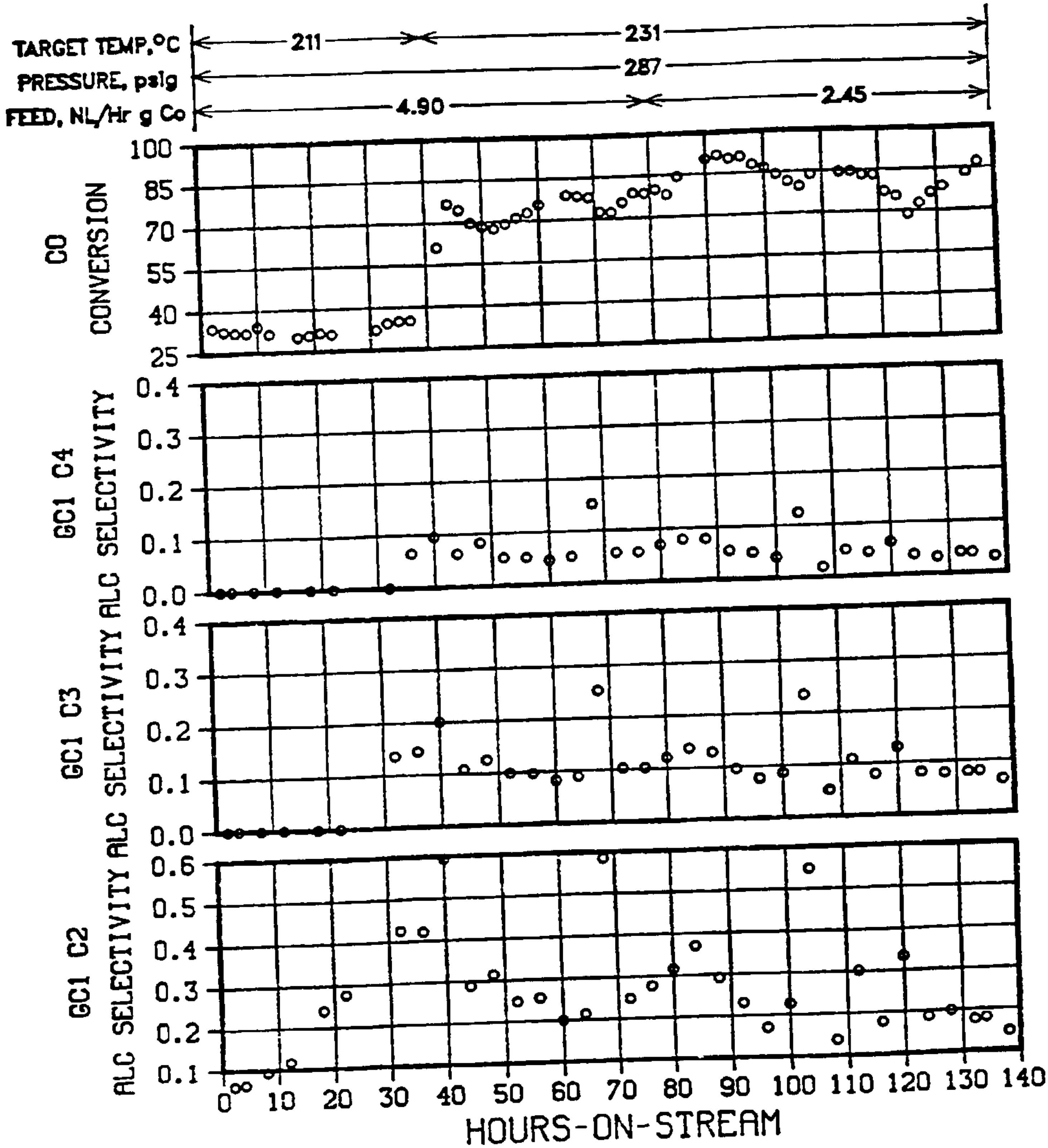

FIGURE A-15
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

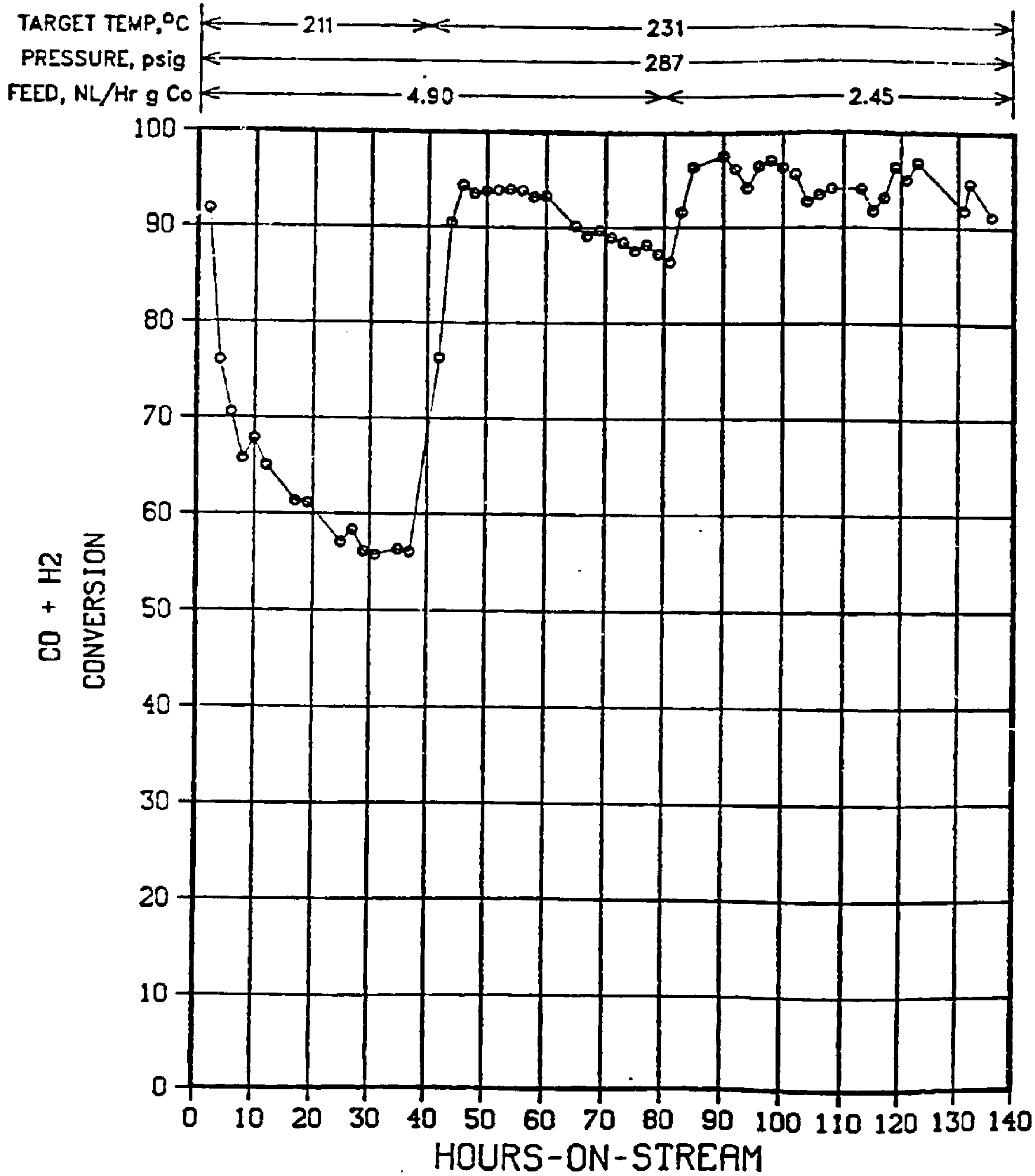

FIGURE A-16
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

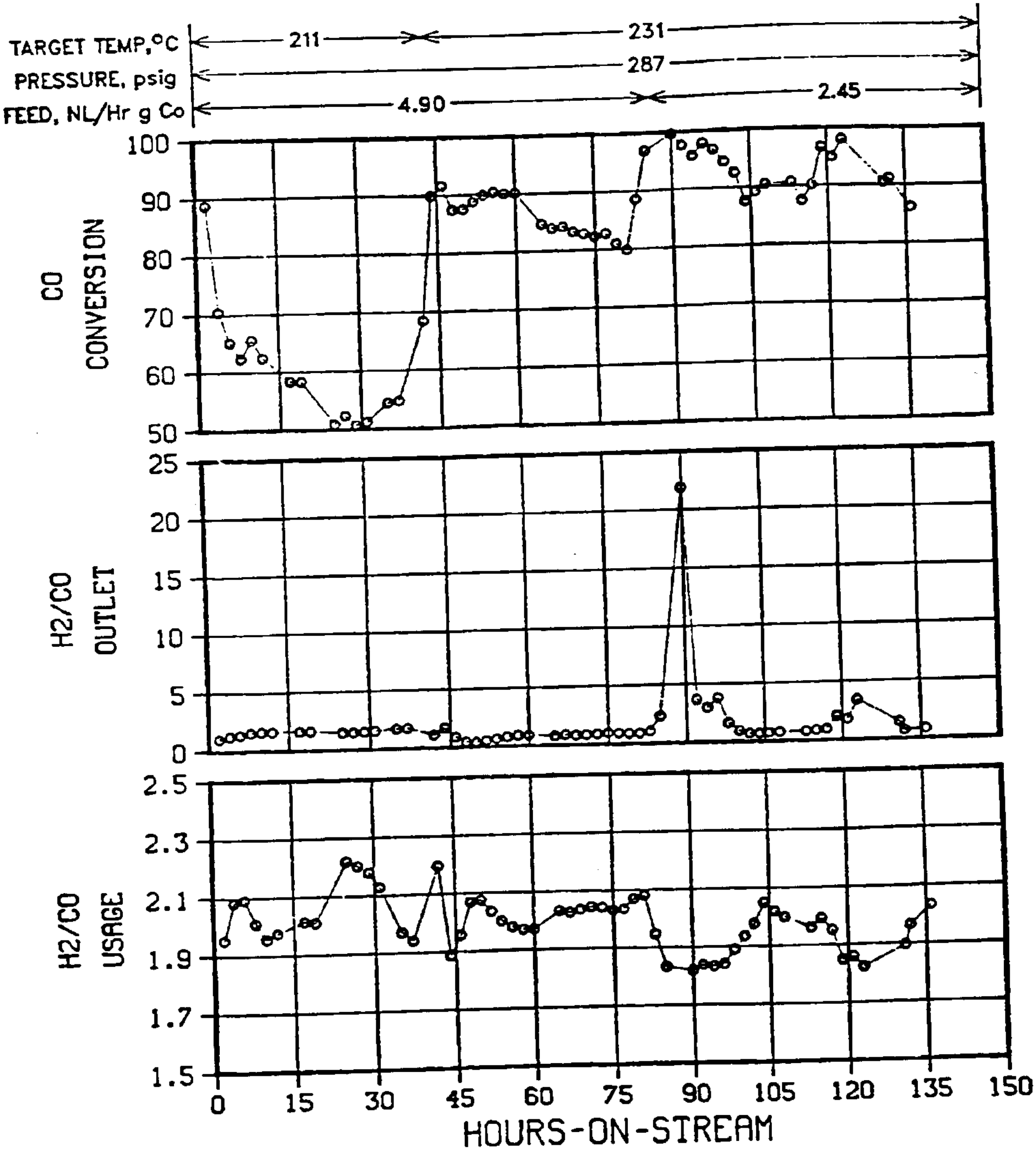

FIGURE A-17
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

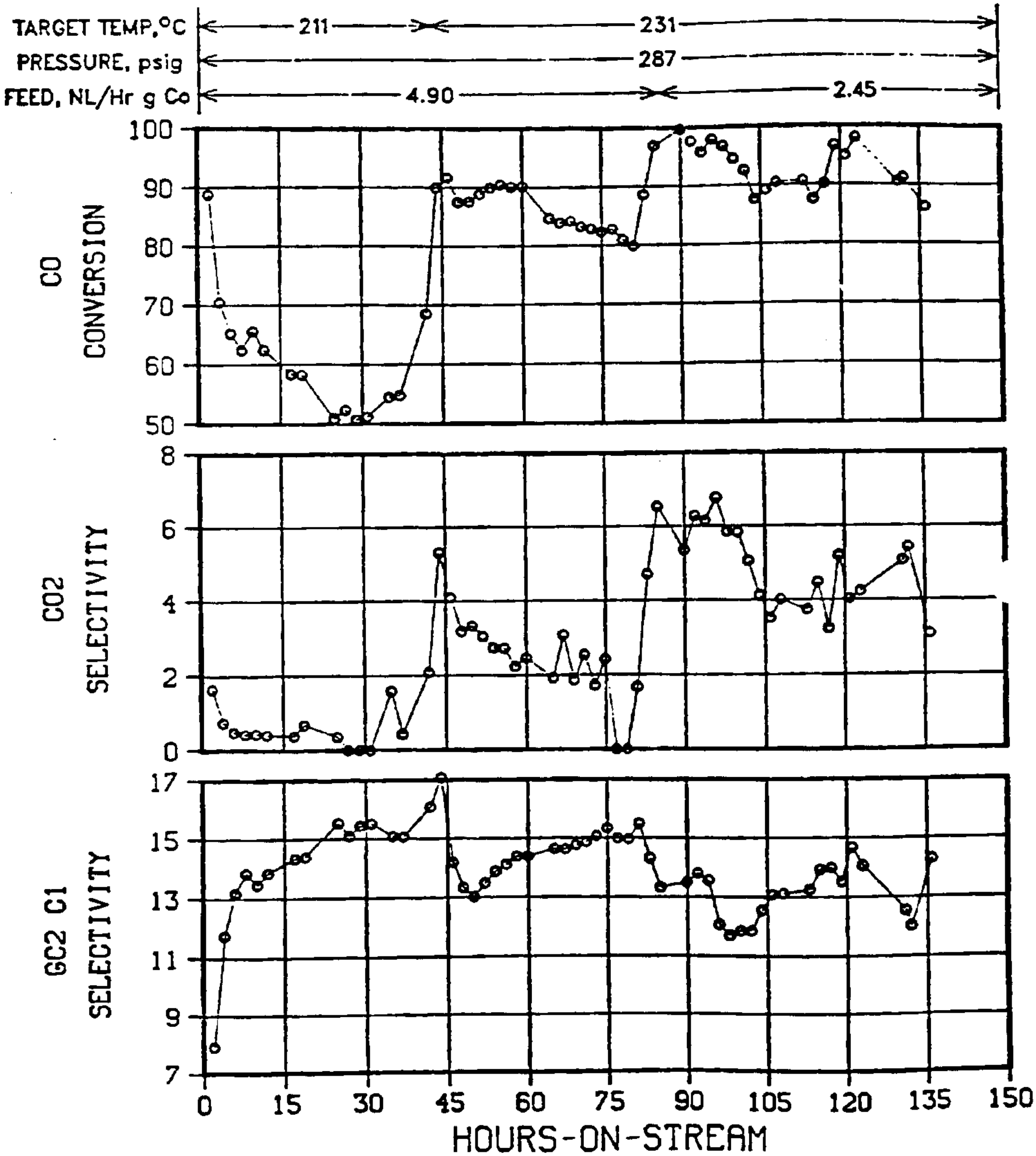

FIGURE A-18
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

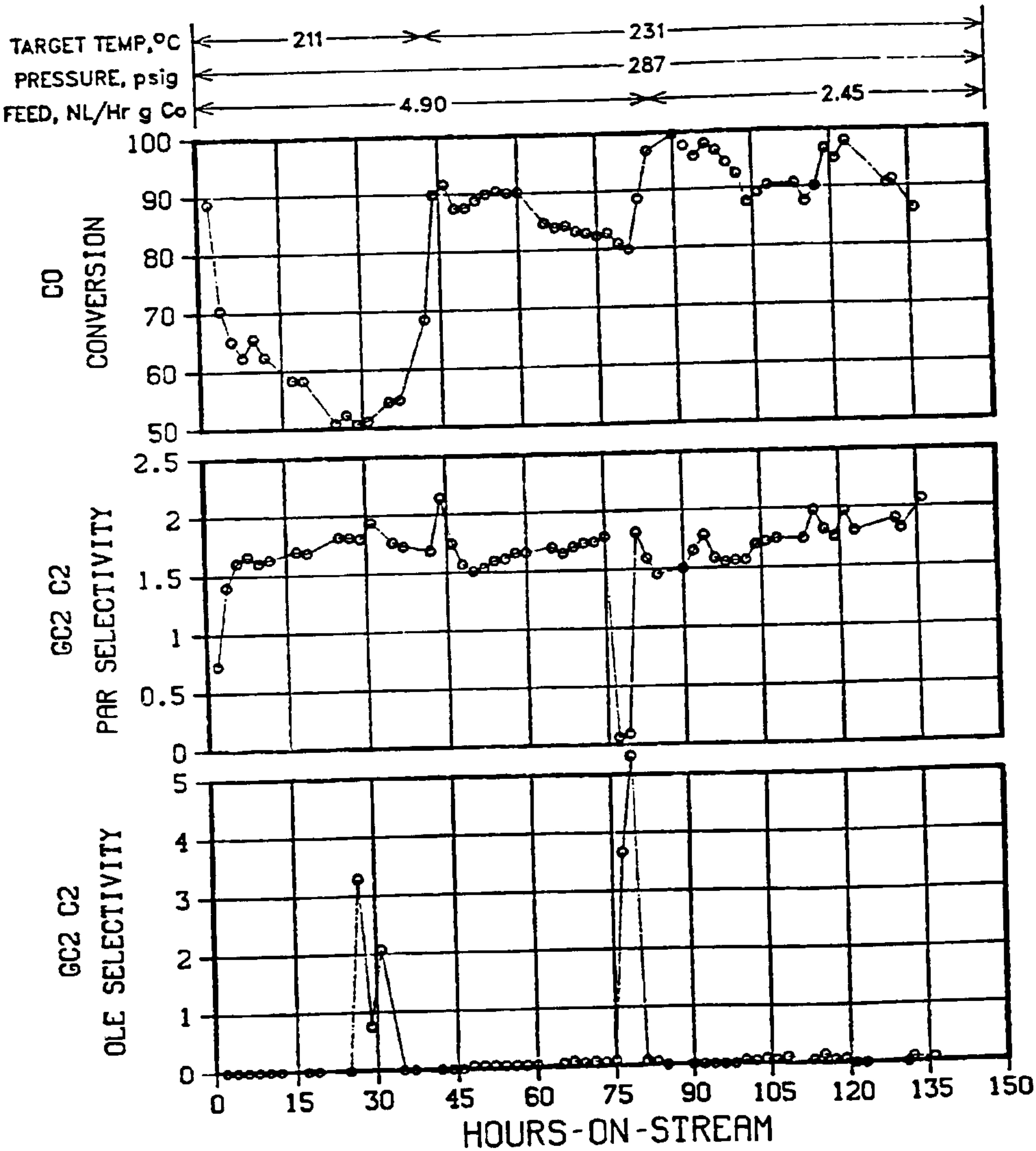

FIGURE A-19
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

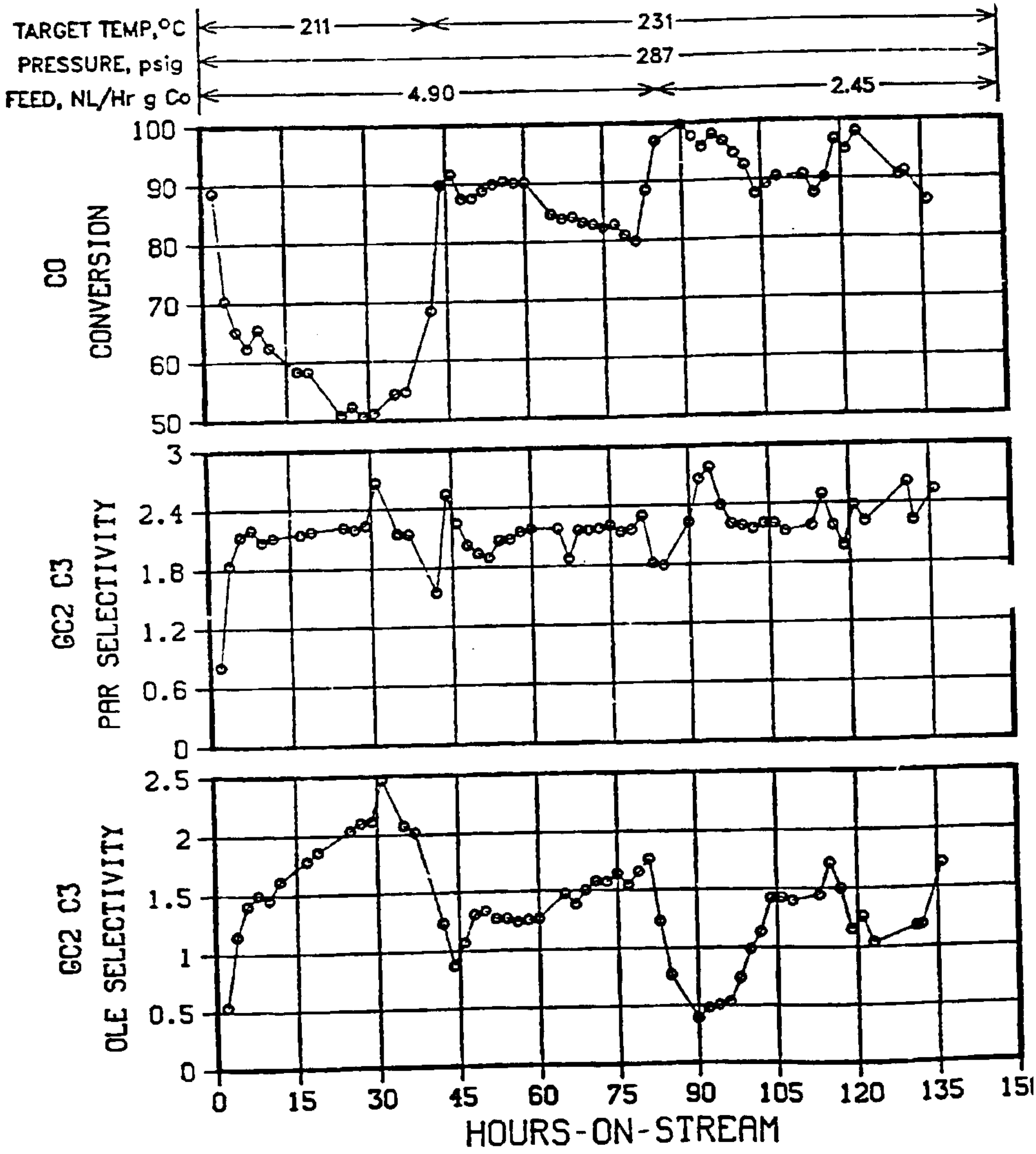

FIGURE A-20
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

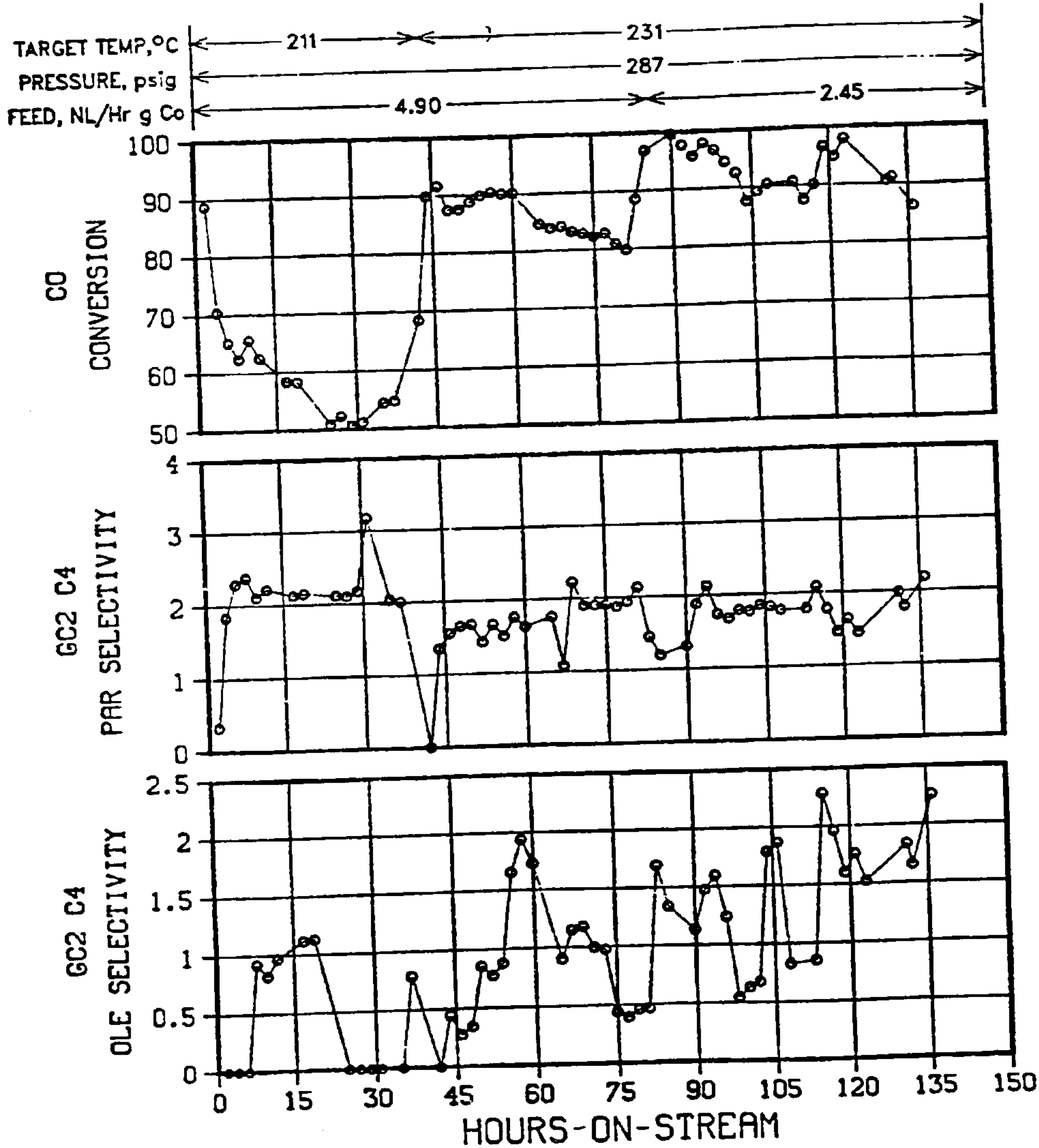

FIGURE A-21
SUMMARY DATA FOR RUN 85 (CATALYST 6531-182)

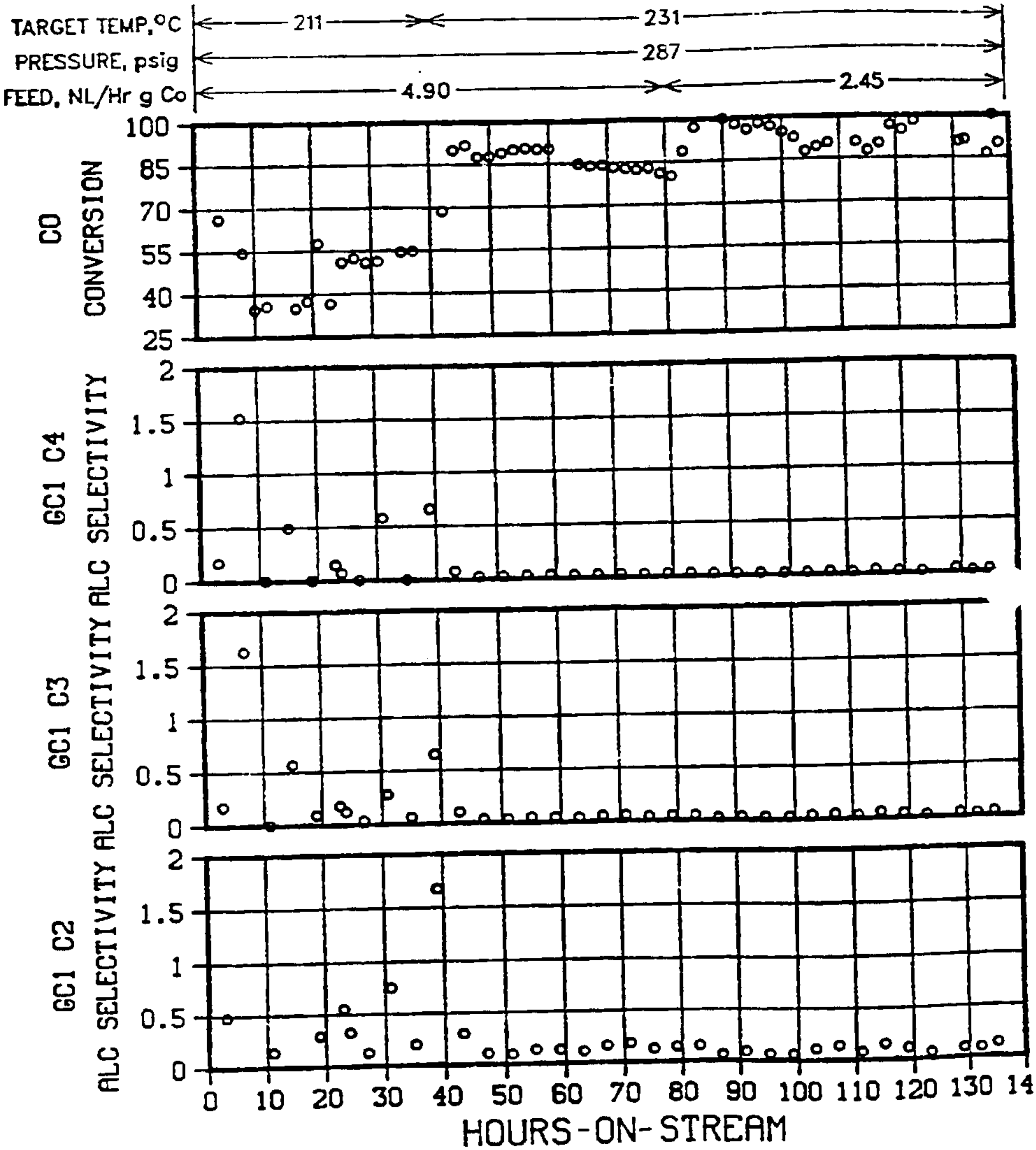

FIGURE A-22
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

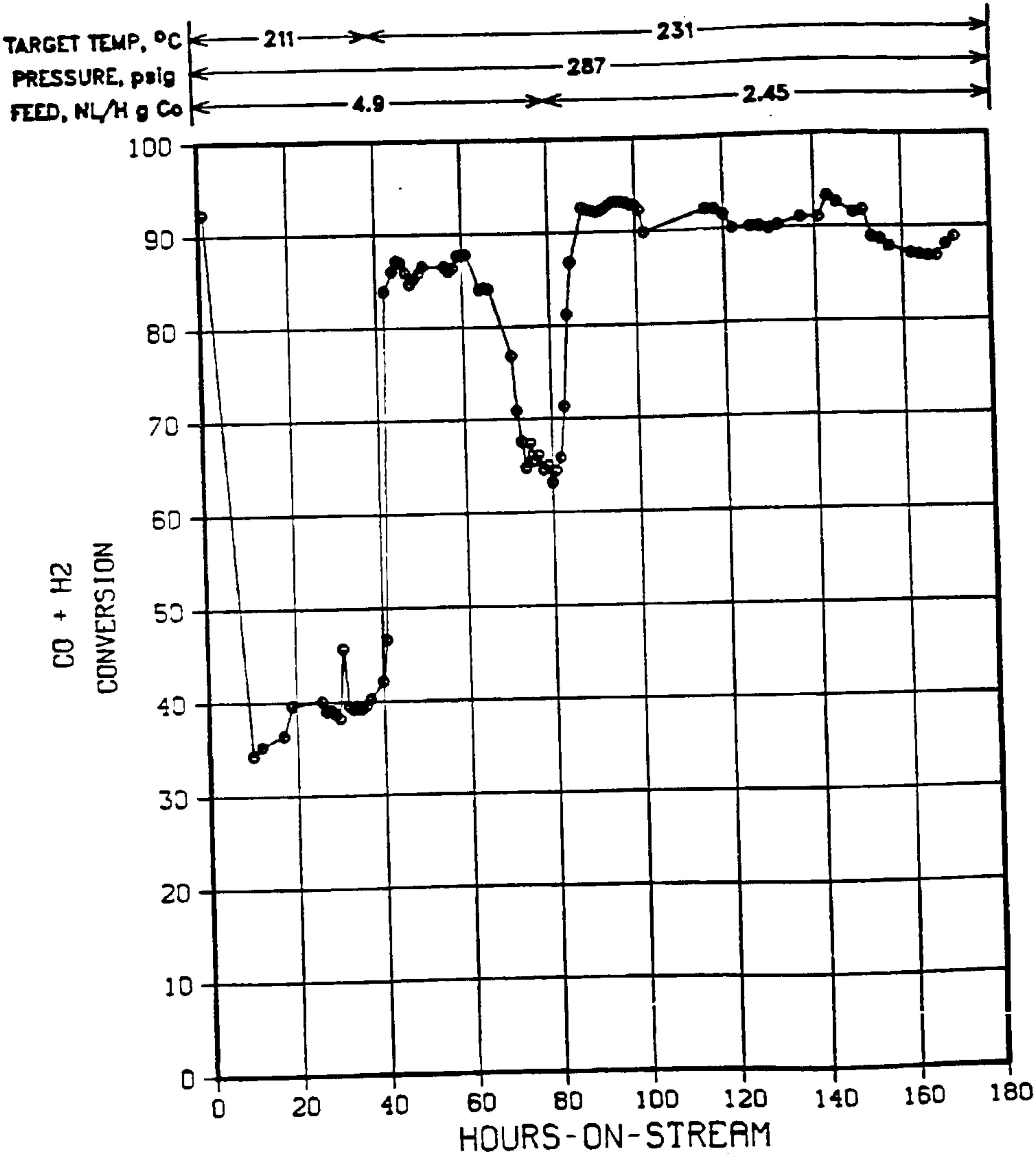

FIGURE A-23
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

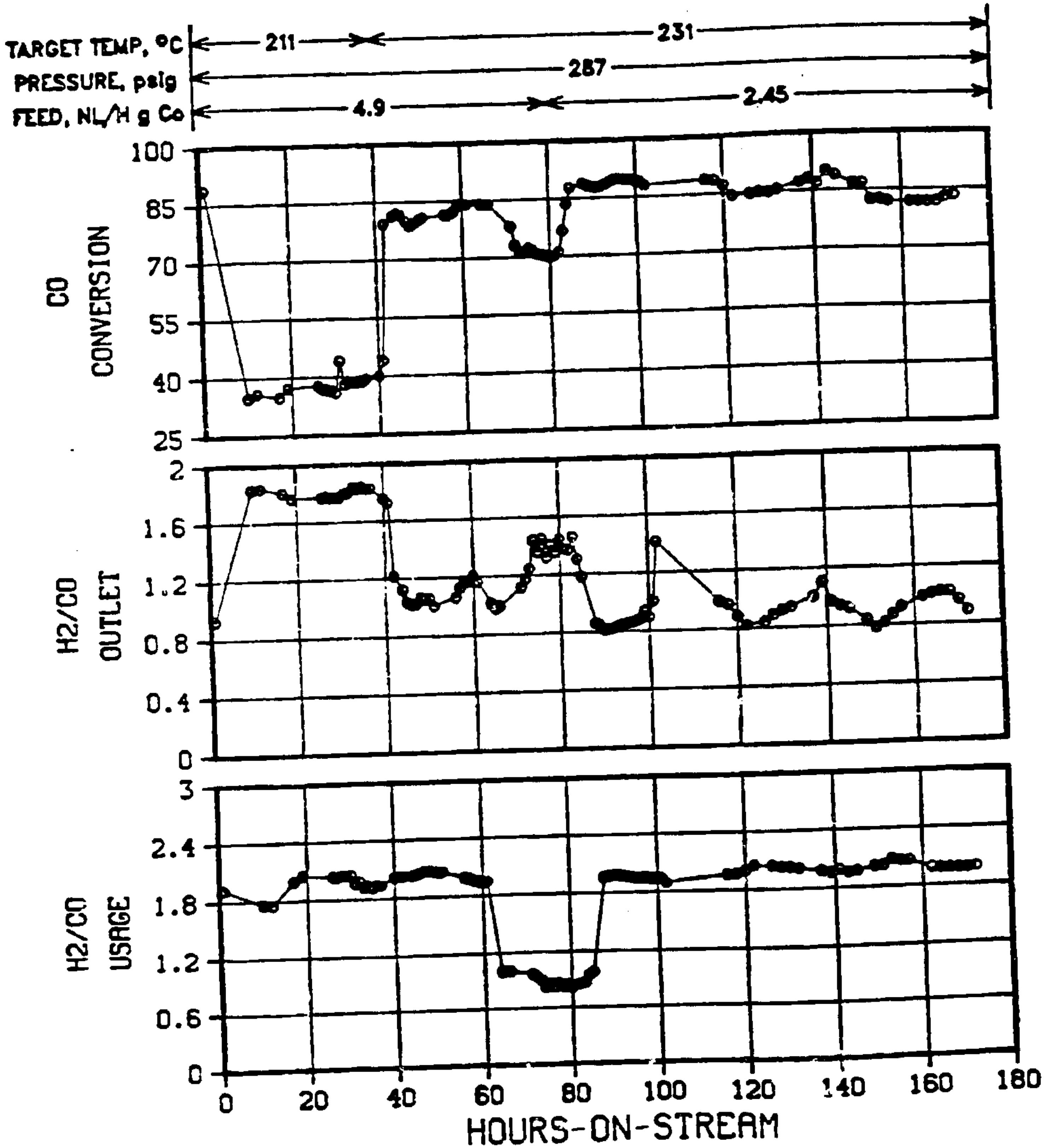

FIGURE A-24
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

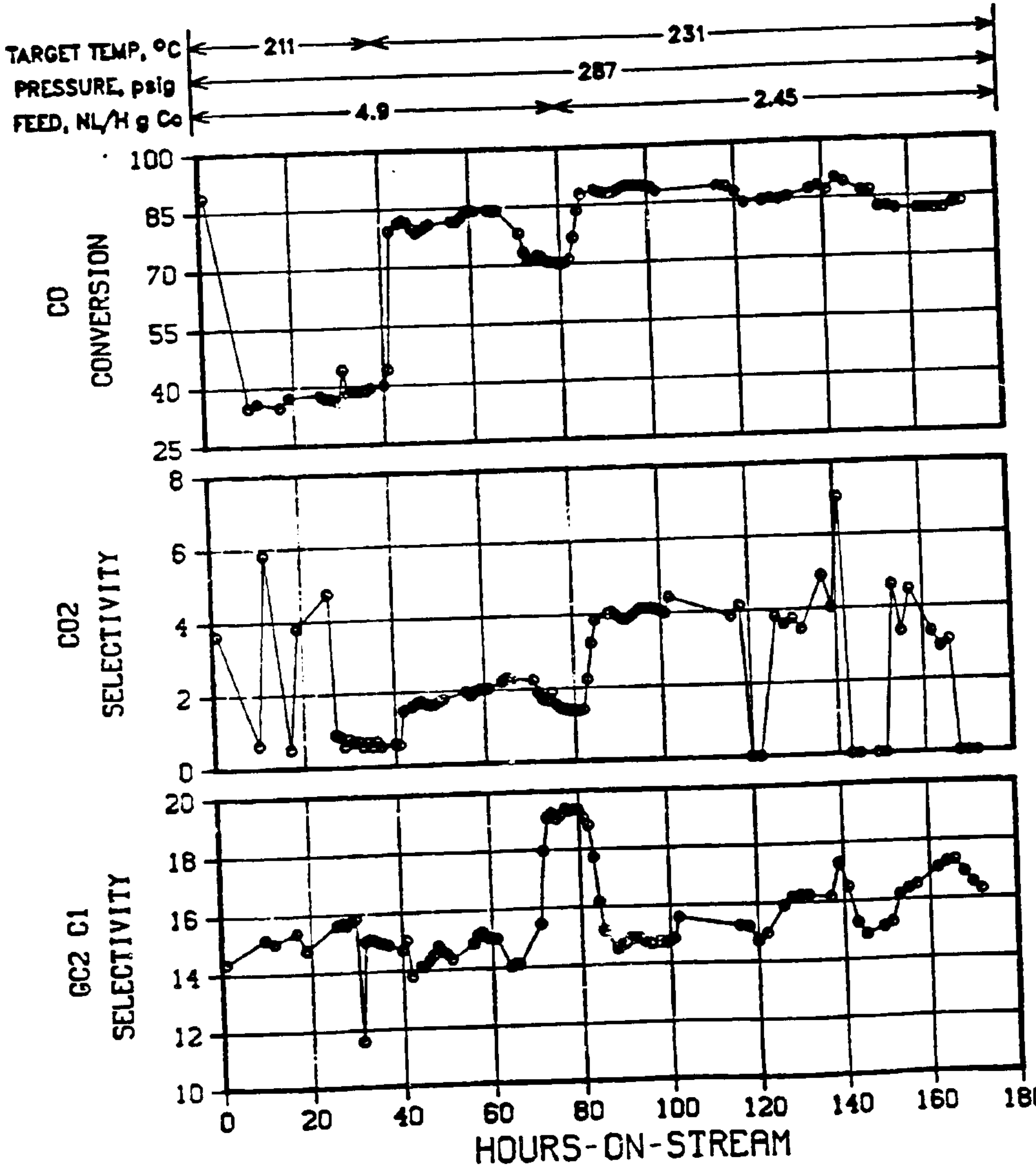

FIGURE A-25
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

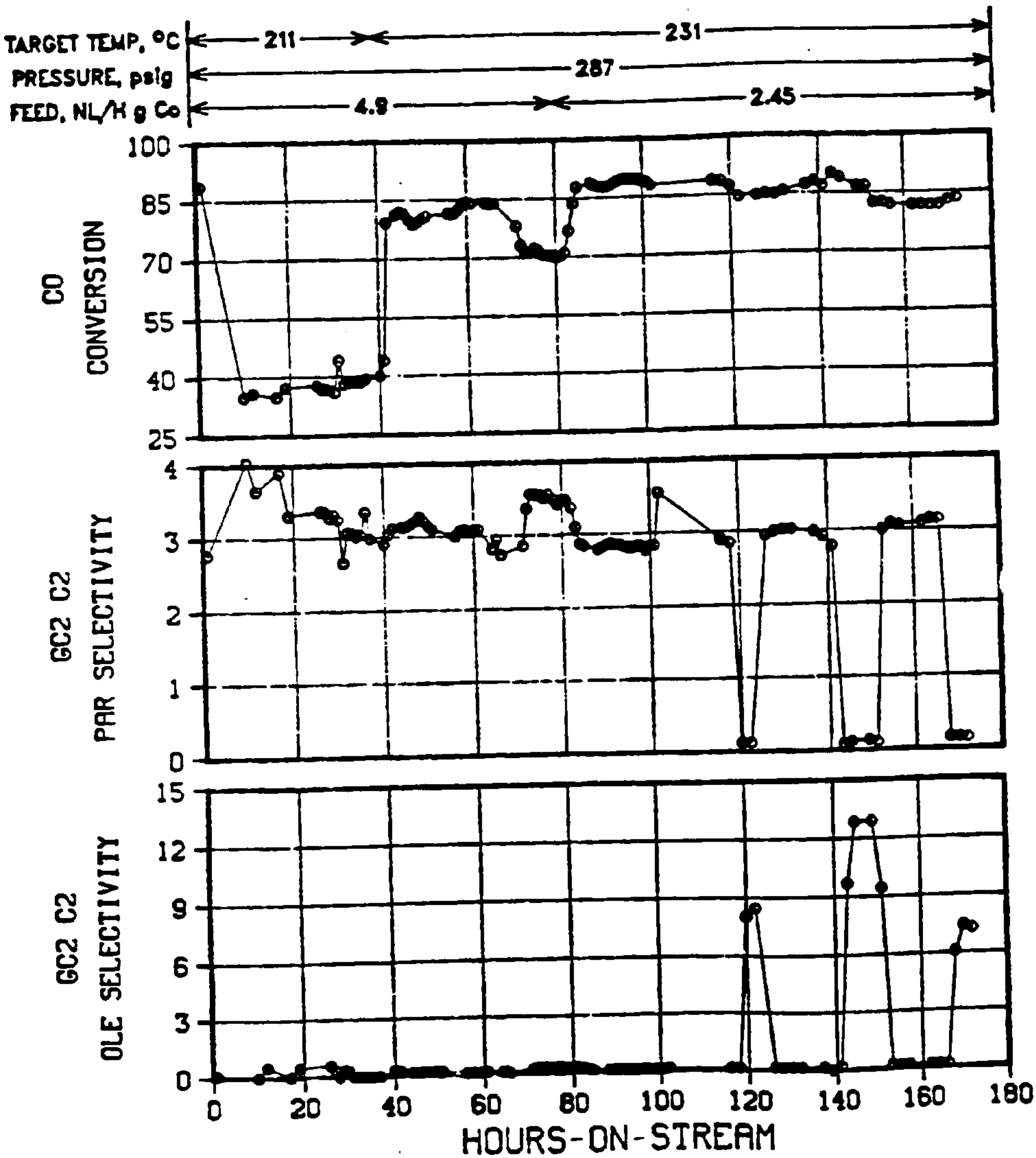

FIGURE A-26
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

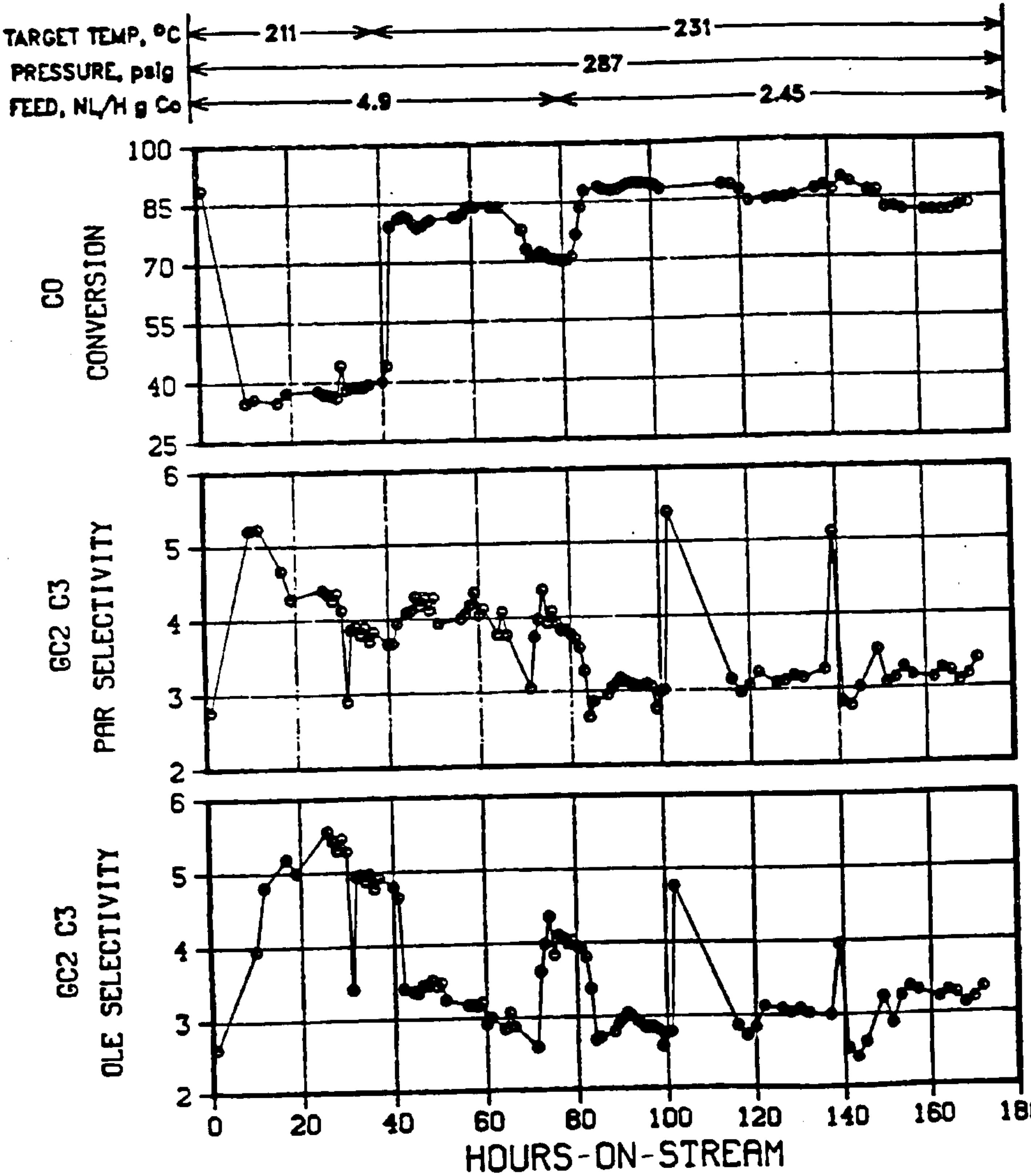

FIGURE A-27
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

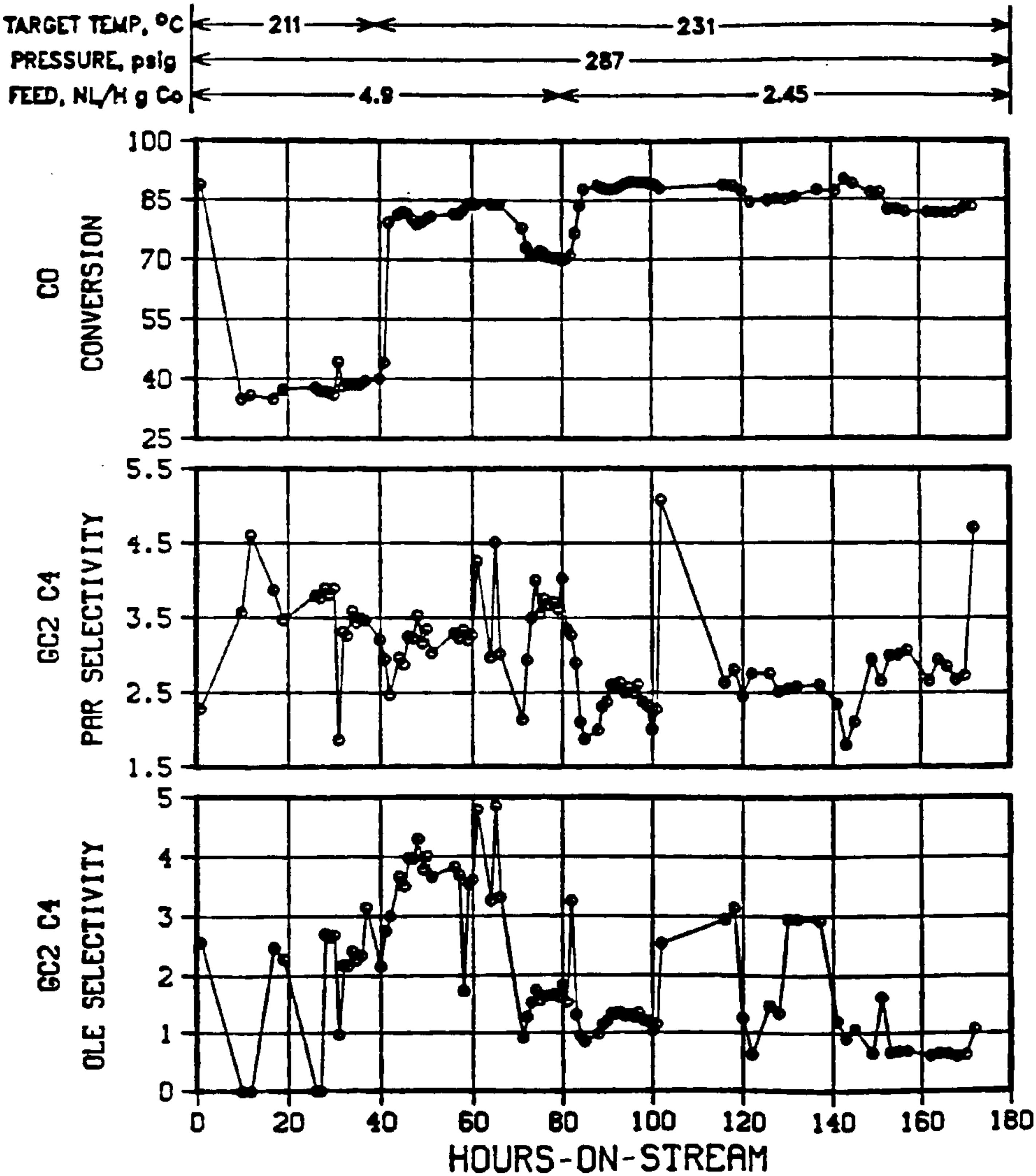

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FIGURE A-28
SUMMARY DATA FOR RUN 86 (CATALYST 6531-188)

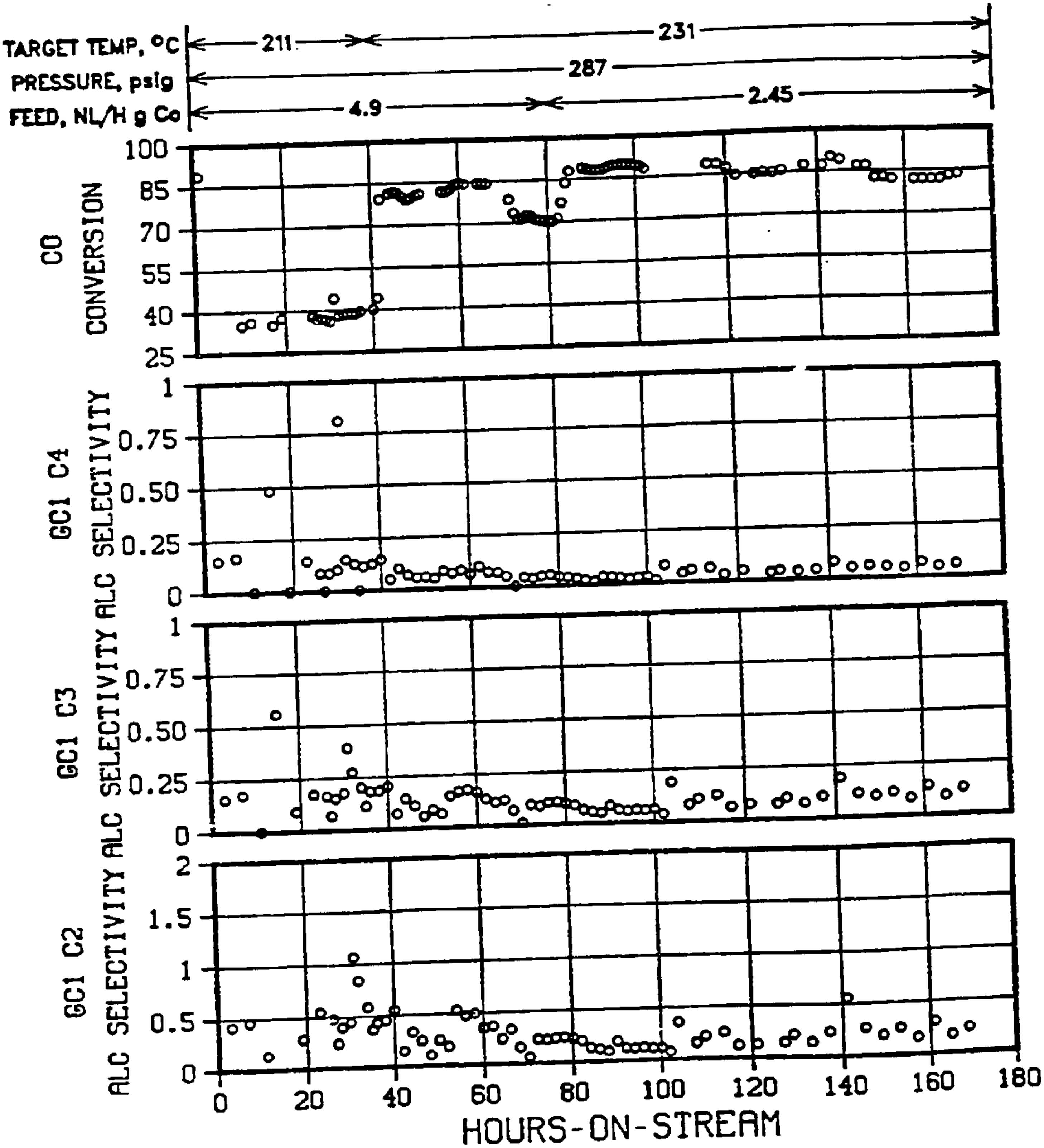

FIGURE A-29
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

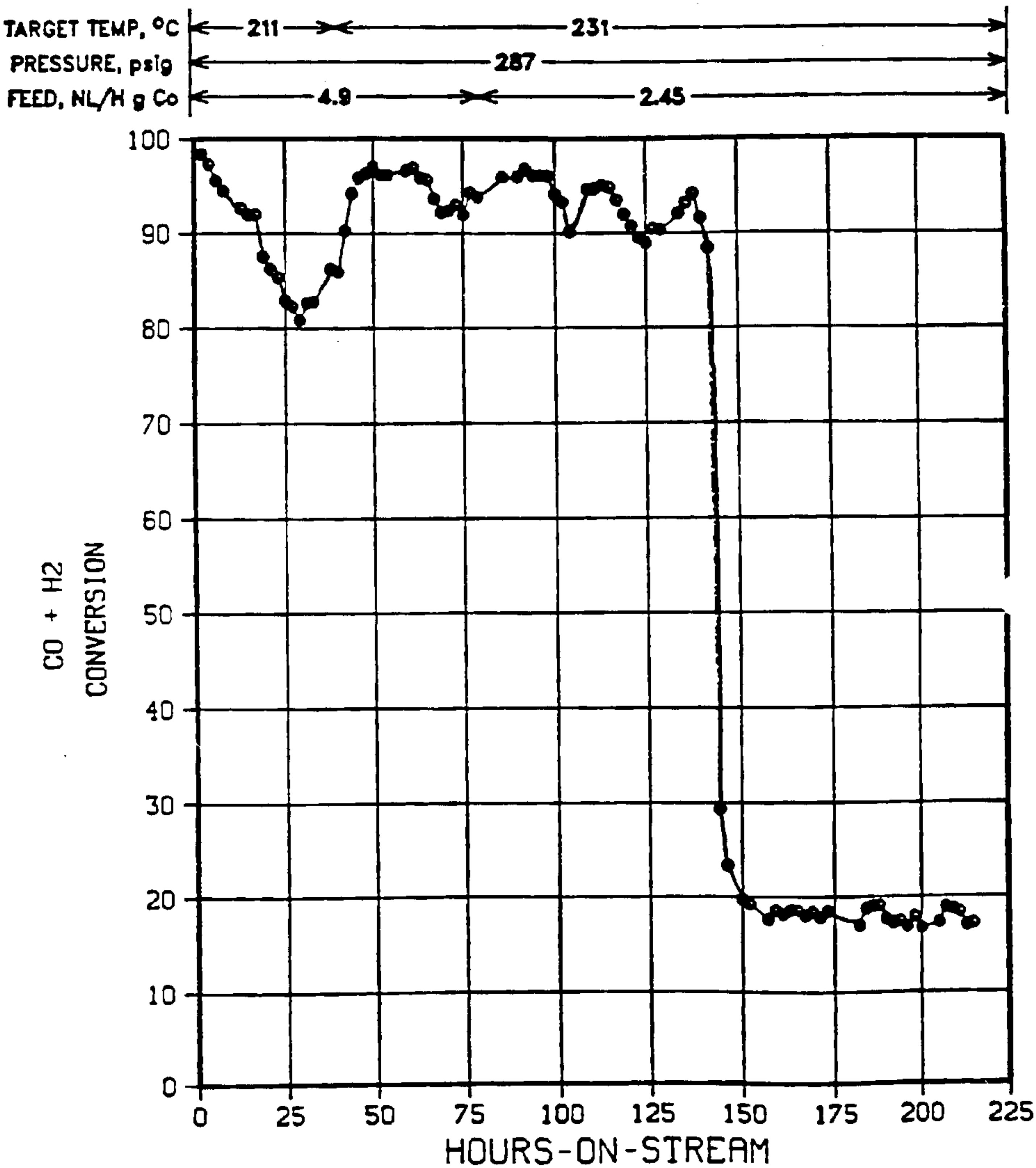

FIGURE A-30
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

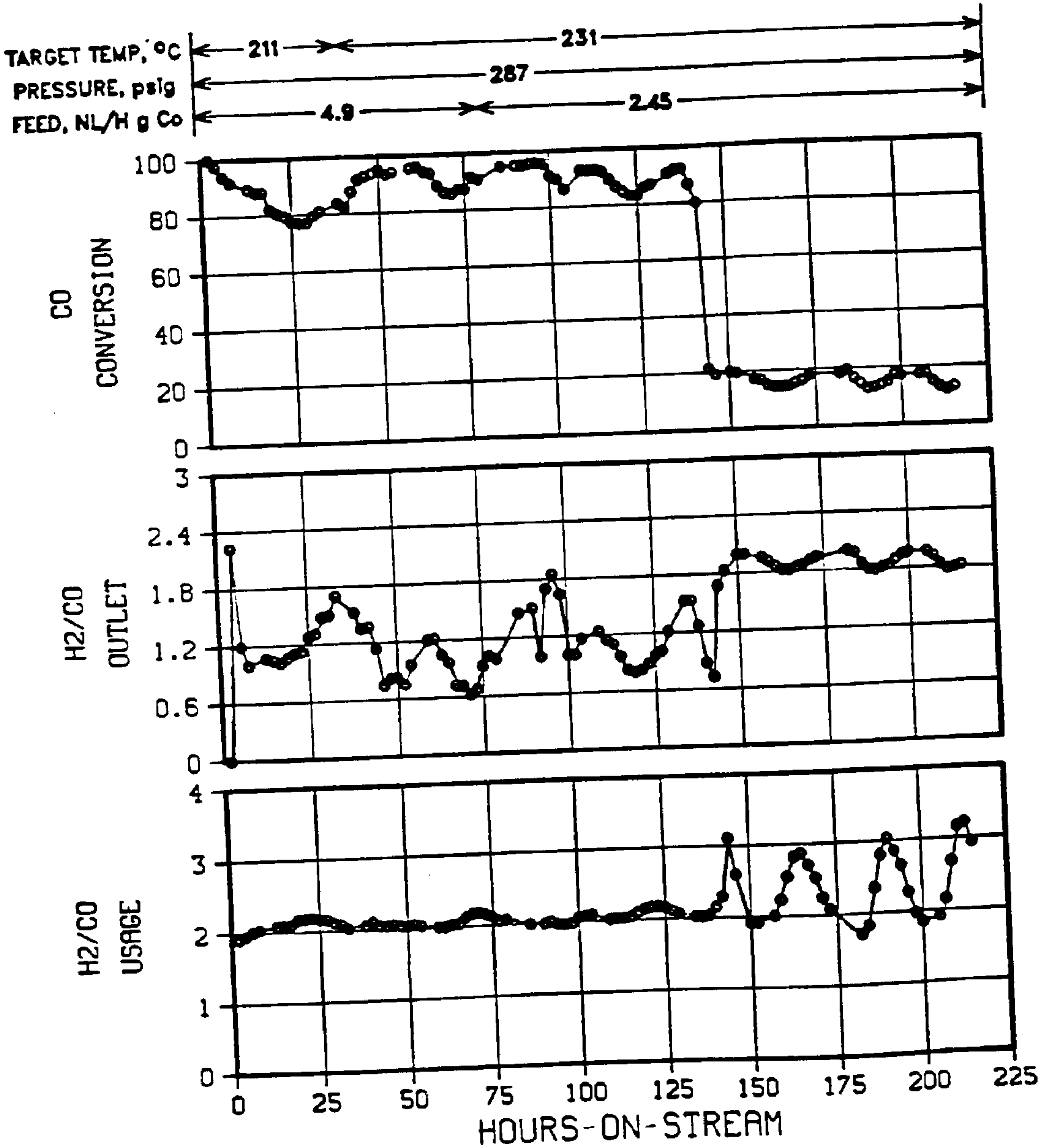

FIGURE A-31
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

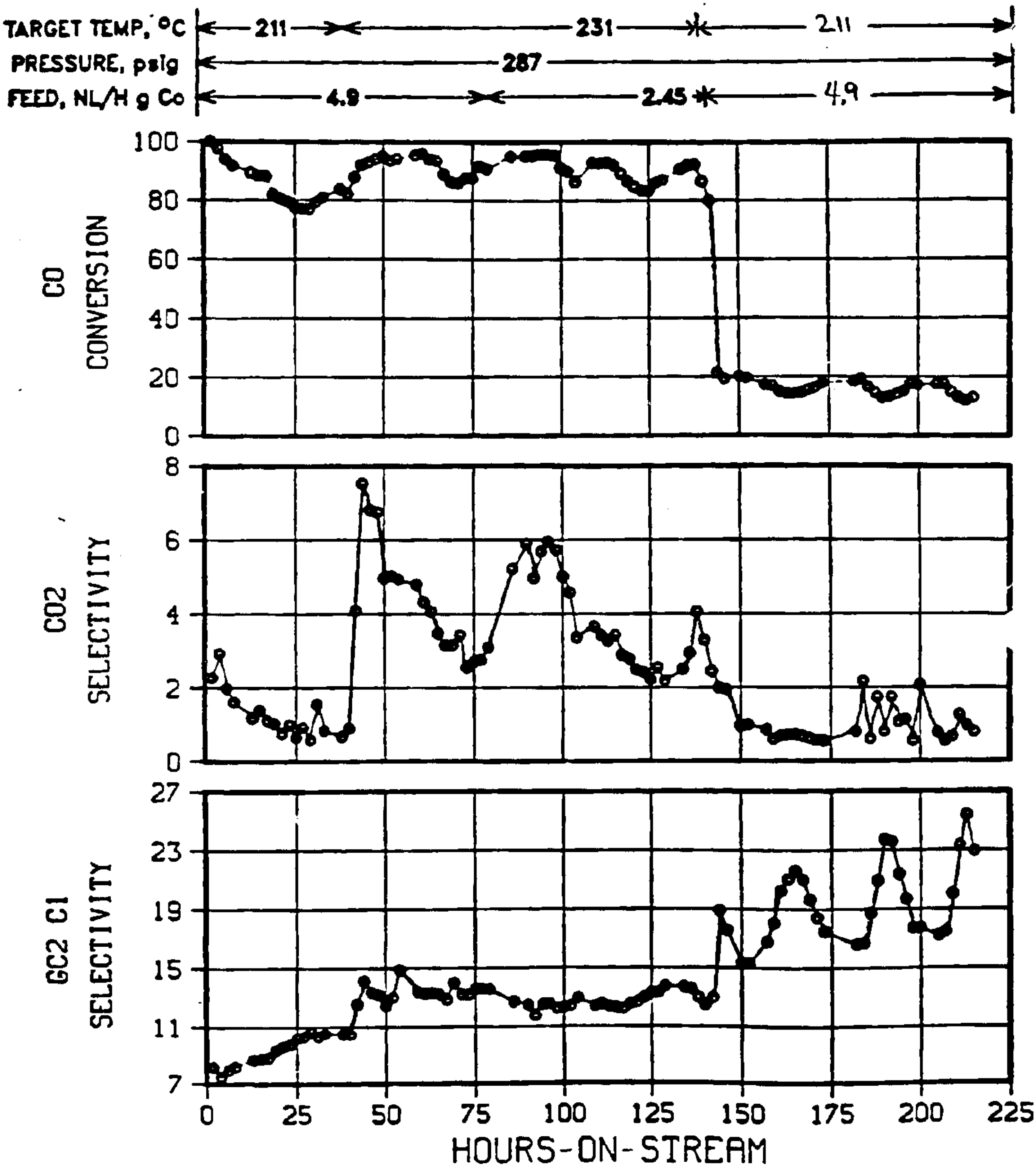

FIGURE A-32
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

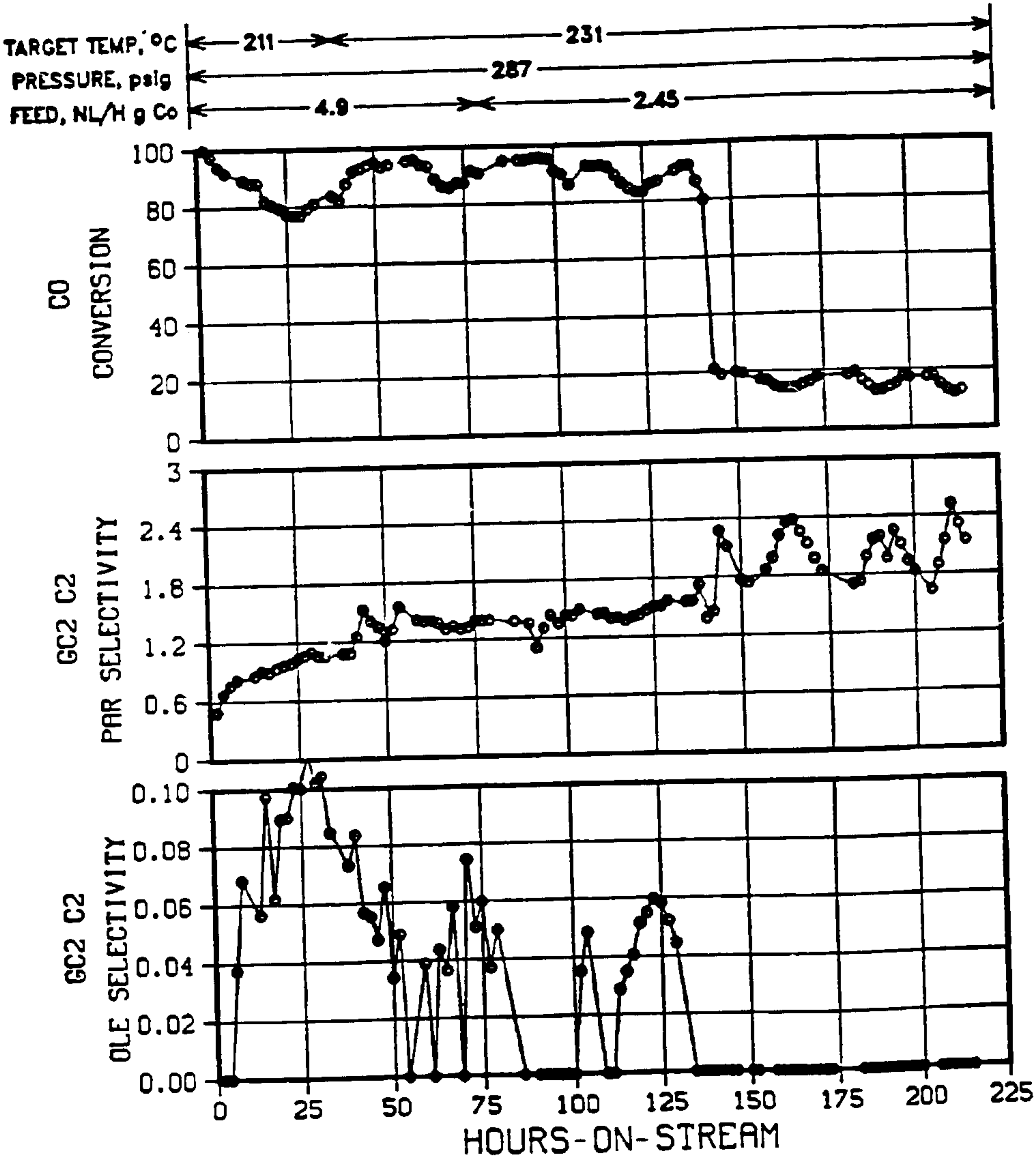

FIGURE A-33
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

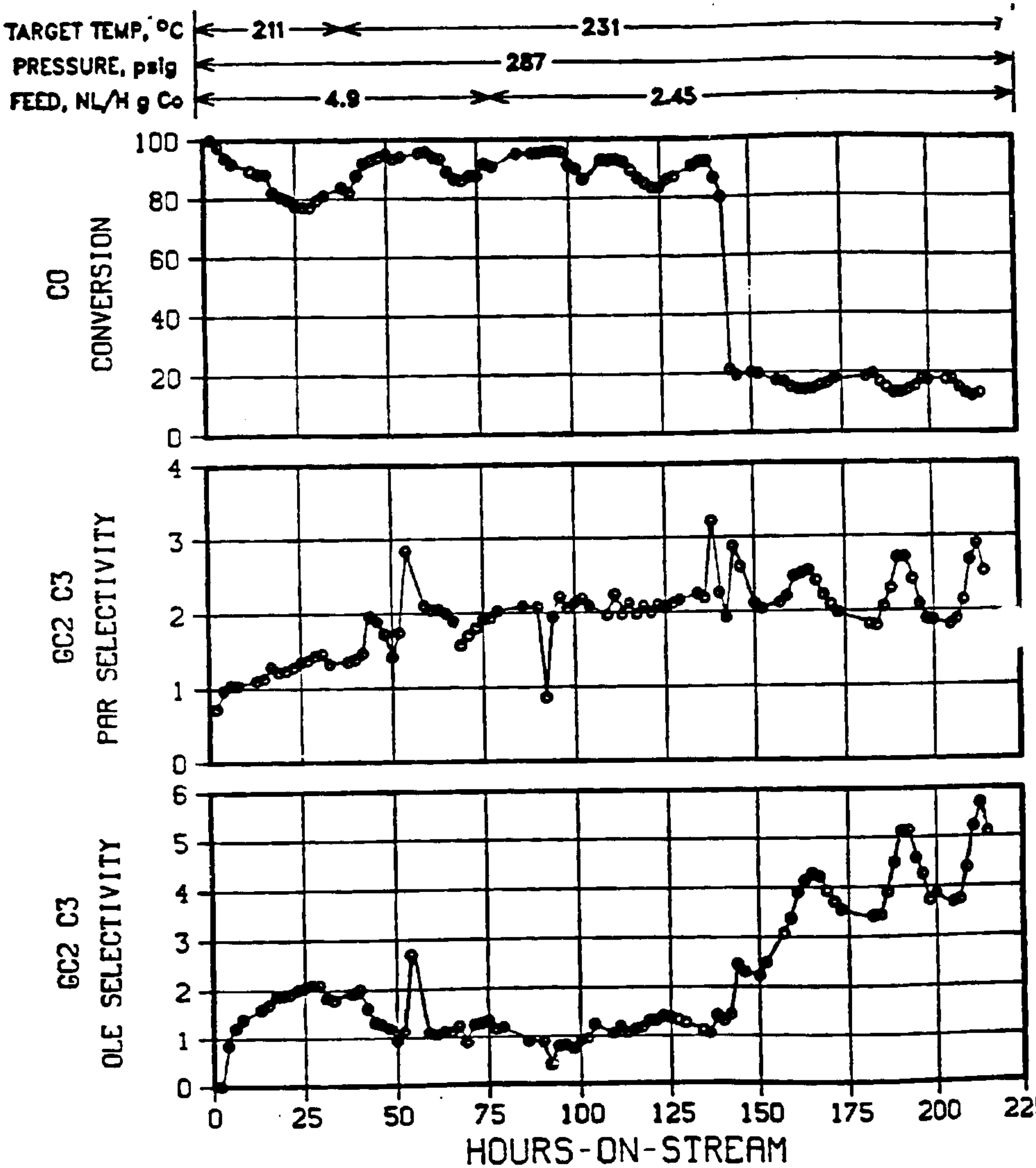

FIGURE A-34
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)

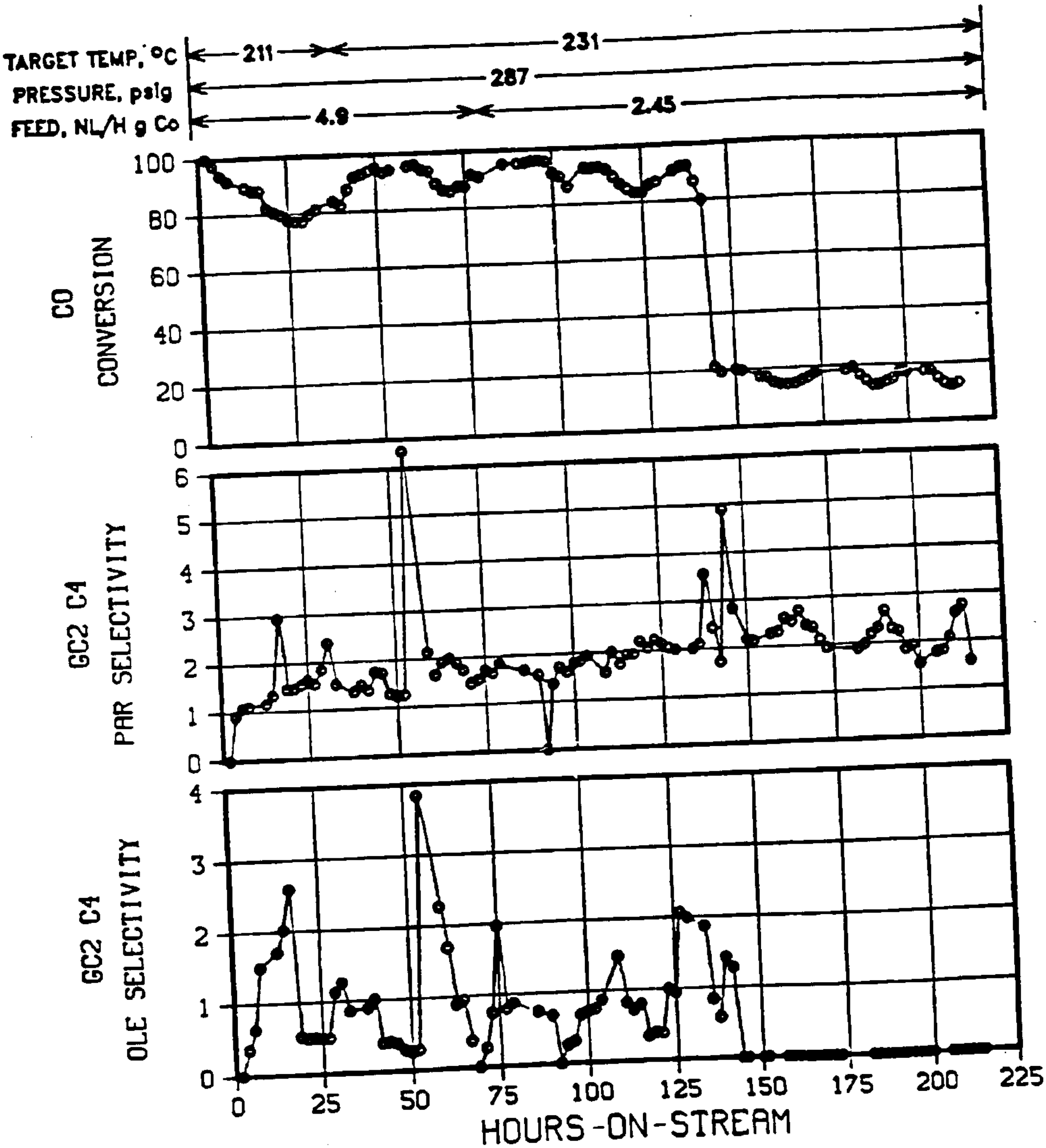

FIGURE A-35
SUMMARY DATA FOR RUN 87 (CATALYST 6531-186)