DOE/PC/89869--T10

89869-T10

DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

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Contract DE-AC22-89PC89869

by

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Technical Progress Report No. 11
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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.

All catalysts were prepared by an aqueous impregnation procedure and the water was then removed by means of a rotary evaporator at 100°C. The precipitate was then calcined at 450°C for four hours. Following calcination, the catalyst and a diluent (usually quartz sand) were loaded into the fixed-bed reactor. The catalyst was then treated with flowing hydrogen at 350°C for two hours to cause reduction of the metals. The purpose of the diluent is to aid transfer of heat from the very exothermic Fischer-Tropsch reaction. This preparation method is summarized in Figure 1.

For all of 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. This will allow for a direct performance comparison with the reference catalyst. Since none of the catalysts were as active as the reference, the second and third 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. One goal of the current work is to develop high activity catalysts which exhibit low methane selectivity.

For catalyst testing runs discussed in this report, run summary plots of conversions and selectivities vs hours-on-stream are attached in Appendix A. Composition of these catalysts is shown in Table 2 and summary performance data are shown in Tables 3 and 4.

Scope of Work During Reporting Period

Four 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 four new catalysts were prepared on a commercial product which is a specially-prepared Y zeolite. A special solvent was used to impregnate metals on to the reference catalyst, whereas the four new catalysts were prepared by aqueous impregnation of metals.

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.

Results and Discussion

Run 78

In addition to ruthenium, the catalyst (No. 6531-167) used in this run contained the same three metals as used in the reference TC 211 catalyst (Co, Mn and Zr). Performance data are summarized as a function of hours-on-stream in Figures A-1 to A-7. At condition 1 this catalyst was less active than the reference catalyst and more selective to methane, both undesirable performance characteristics. At condition 2 a slightly higher conversion resulted than that observed for the reference catalyst at condition 1; however, the methane selectivity was much higher. A further conversion gain was noted going from condition 2 to condition 3; however, methane selectivity did not decrease as much as one would have expected (Table 3).

Run 80

The catalyst (No. 6531-166) used in this run contained only cobalt (see Table 2). Performance data for this catalyst are summarized as a function of hours-on-stream in Figures A-8 to A-14. This catalyst was more active and less selective to methane than the catalyst 6531-167 at all three conditions. This was not expected since manganese is expected to mitigate for lower methane selectivity and ruthenium for greater activity.

Runs 81 and 82

Runs 81 and 82 used similar catalysts, No. 6531-175 and 6531-176, respectively. The metals present and the amounts of these metals were about the same as on the reference catalyst TC 211 (Table 2). Performance data for these two runs as a function of hours on stream are shown in Figures A-15 to A-28. These catalysts performed similarly to catalyst 6531-166 tested in Run 80. They exhibited about the same conversion and methane selectivity at each condition, but were slightly more selective for ethane.

Summary and Implications for Further Work

Four catalysts were prepared by aqueous impregnation on a commercial sample of a specially prepared Y zeolite (591 m^2/g; 0.51 cc/g). These catalysts were evaluated by a quick screening test and compared to a reference catalyst (TC 211) which was developed under a previous DOE contract to a division of Union Carbide which is now part of UOP. Catalyst TC 211 was prepared by impregnating metals onto a laboratory steamed and acid-washed Y zeolite. A special impregnation solvent was used. At similar operating conditions, the four catalysts tested were less active and more selective to methane than the reference catalyst. A temperature change was made in the testing of these four catalysts (condition 1 to condition 2) to obtain conversions comparable to that obtained with the reference catalyst. Higher methane selectivity was noted for these catalysts when comparisons were made at similar conversion levels. When the new catalysts were evaluated at different conversions resulting from changes in feed rate at the same temperature (condition 2 to condition 3) high methane selectivity persisted. Thus these catalysts did not exhibit the expected lower methane selectivity at higher conversion. The four catalysts tested were intrinsically more selective to methane than the reference catalyst. They were, however, similar to the reference catalyst in their low selectivity to alcohols (Table 5). Of the four catalysts, catalyst 6531-167 which contained ruthenium appeared to be the most selective for methane.

Attempts will be made to prepare more active and less methane selective catalysts. The next round of catalysts will be prepared on the same commercial support, but laboratory acid washing will be performed prior to impregnation. It is possible that catalyst TC 211 was prepared on a more extensively washed support than the current catalyst prepared on the commercial Y-zeolite support. Additionally, the special impregnation solvent used in the preparation of catalyst TC 211 will be used in this preparations.

Table 1
Operating Conditions for the Three Condition Test

	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
Composition of Catalyst Precursors by Atomic Absorption Spectroscopy

Run No.	*Catalyst No.*	*Support*	*AAS, wt-%*
65	*TC 211*	*Steamed, acid-washed Y zeolite*	*Co, 8.3; Mn, 1.3; Zr, 1.0*
81[1]	*6531-167*	*Steamed Y zeolite*[2]	*Co, 8.1; Mn, 0.36; Zr, 1.0*
82[1]	*6531-166*	*Steamed Y zeolite*[2]	*Co, 7.3; Mn, 0.64; Zr, 0.99*
78[1]	*6531-175*	*Steamed Y zeolite*[2]	*Co, 7.3; Ru, 1.2; Mn, 0.6; Zr, 1.0*
80[1]	*6531-176*	*Steamed Y zeolite*[2]	*Co, 7.5*

[1] *Aqueous impregnation*
[2] *SA = 591 m^2/g; Pore volume = 51 cc/g*

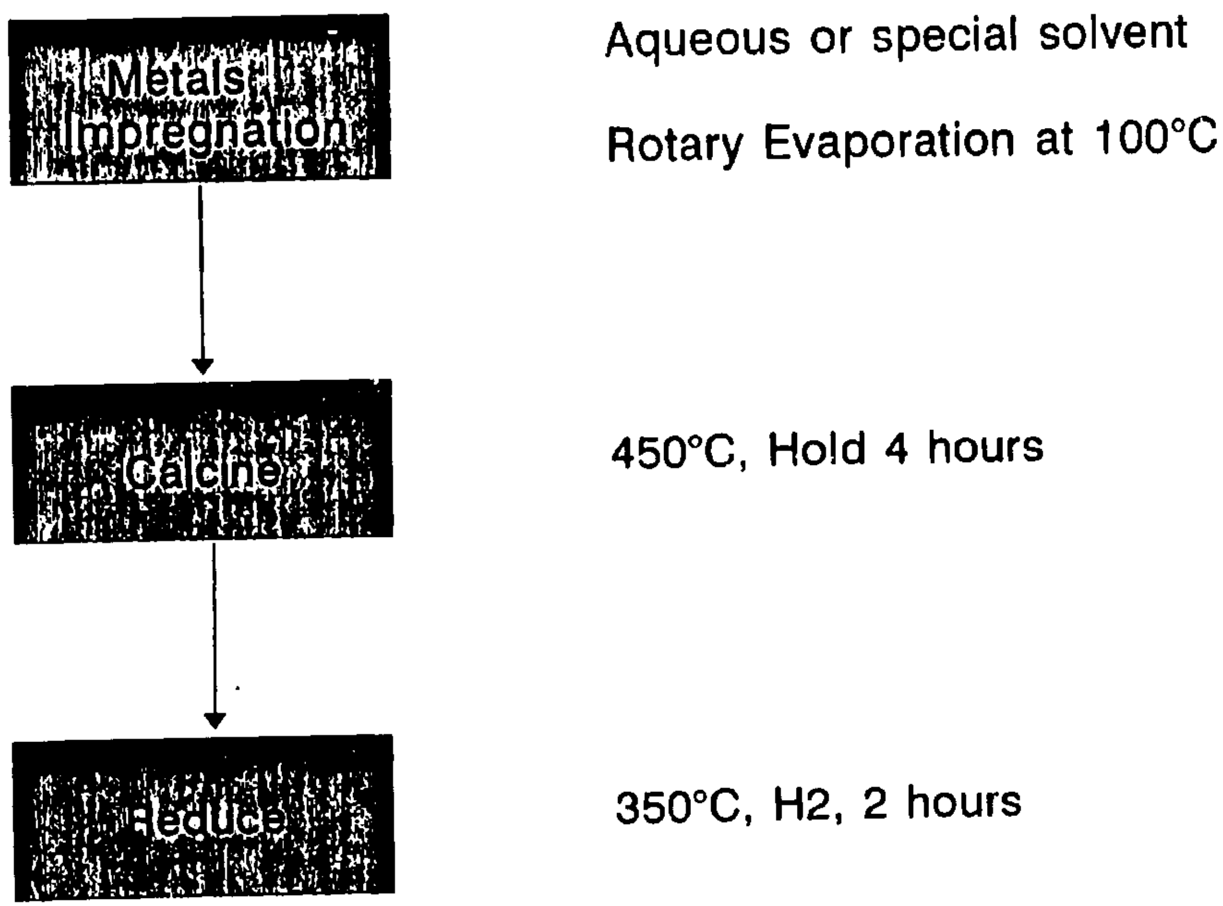
Table 3
Activity and Hydrocarbon Selectivity of Catalysts

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
81	1	35	18	3.2	0	4.0	3.0
	2	78	17	2.8	0.2	5.0	2.1
	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
78	1	35	24	5.0	2.0	4.8	1.5
	2	65	30	2.2	0	4.9	1.6
	3	80	27	2.2	0	5.0	1.3
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

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
81	1	35	0	0	0
	2	78	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
78	1	35	0.4	0	0
	2	65	0.3	0.06	0.04
	3	80	0.2	0.06	0.06
80	1	41	0.1	0	0
	2	77	0.1	0.03	0.01
	3	86	0.1	0.02	0.01

Figure 1
Standard Catalyst Preparation



APPENDIX A

CATALYST PERFORMANCE DATA RUN SUMMARY

FIGURE A-1
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

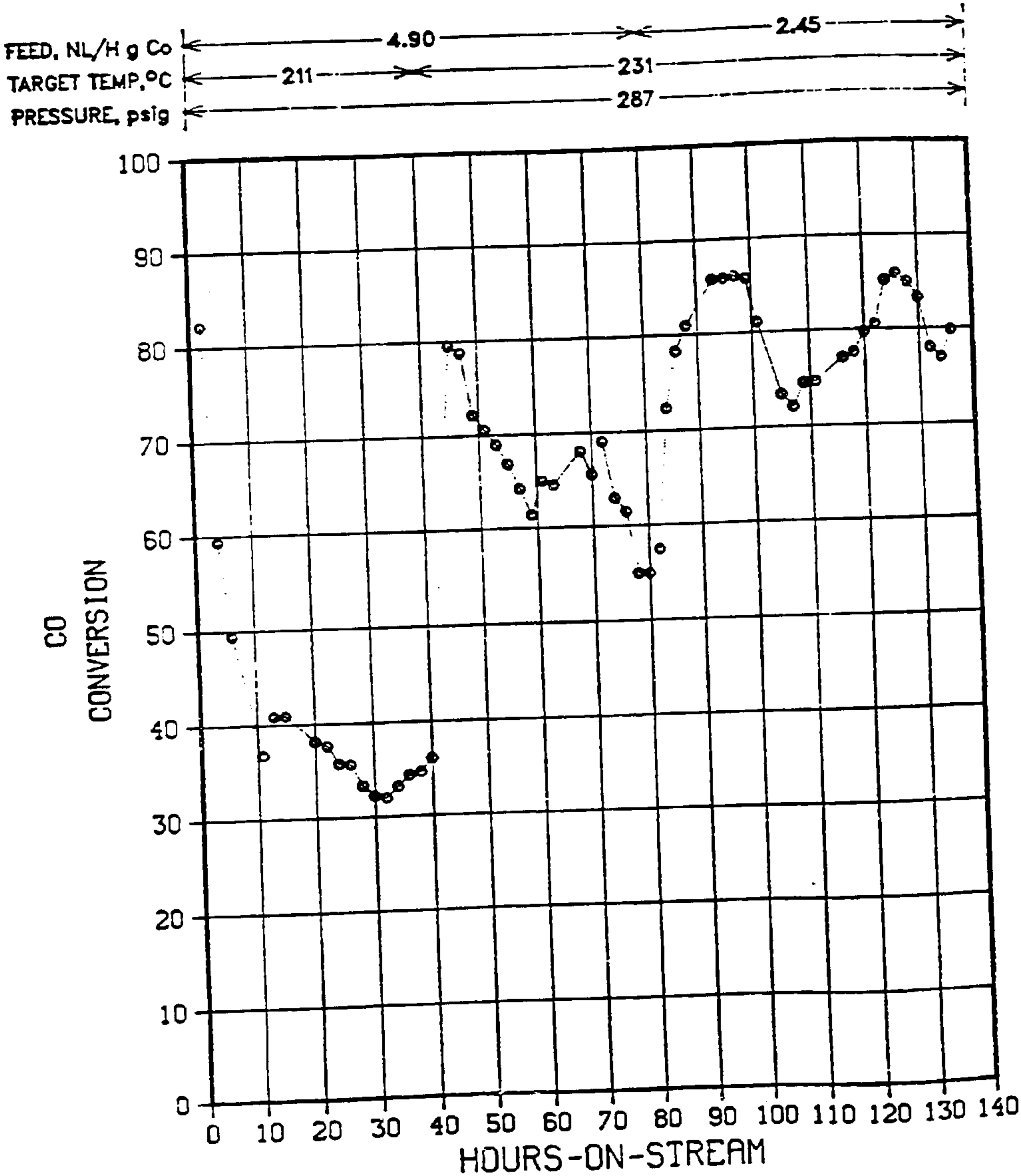


FIGURE A-2
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

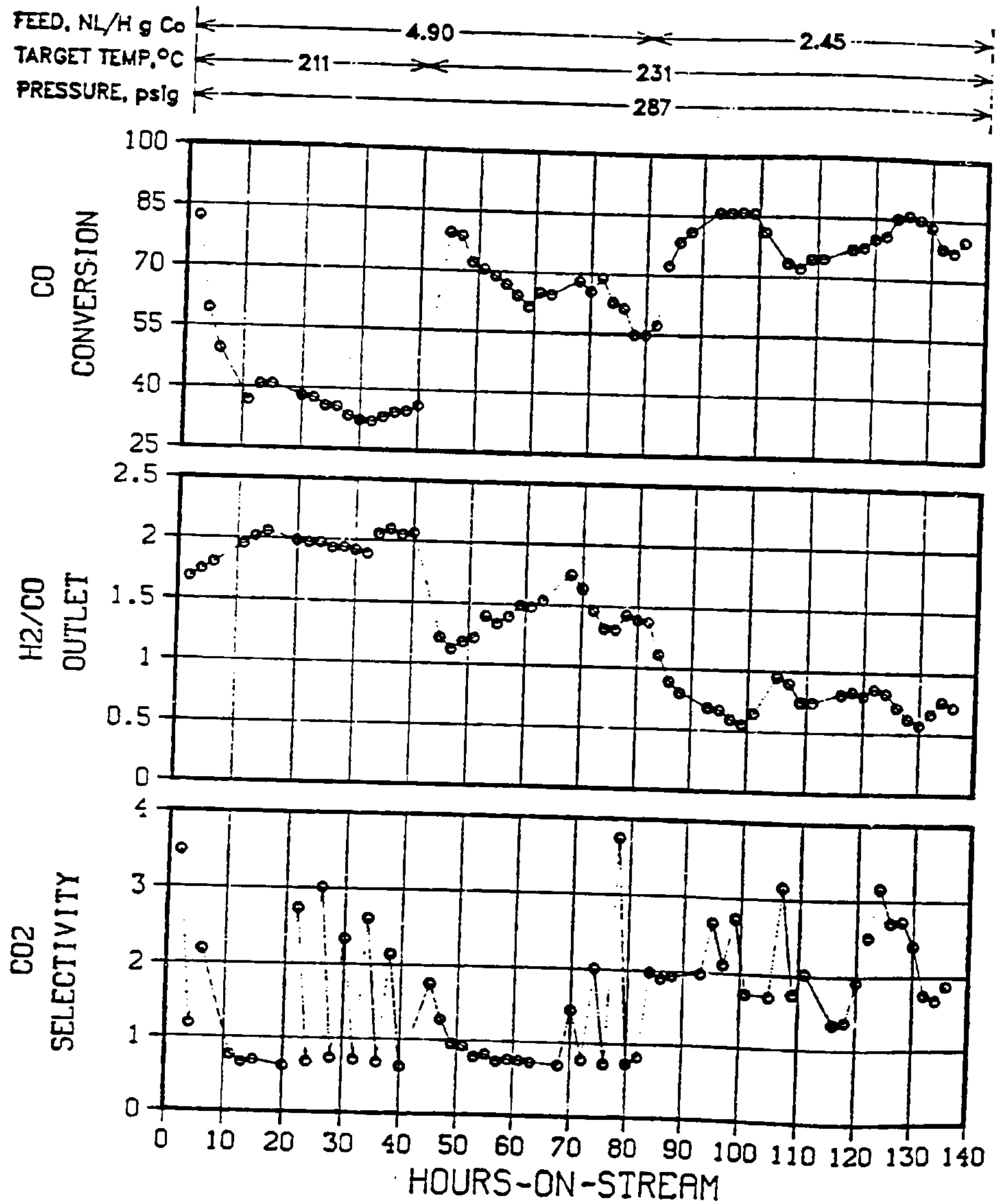


FIGURE A-3
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

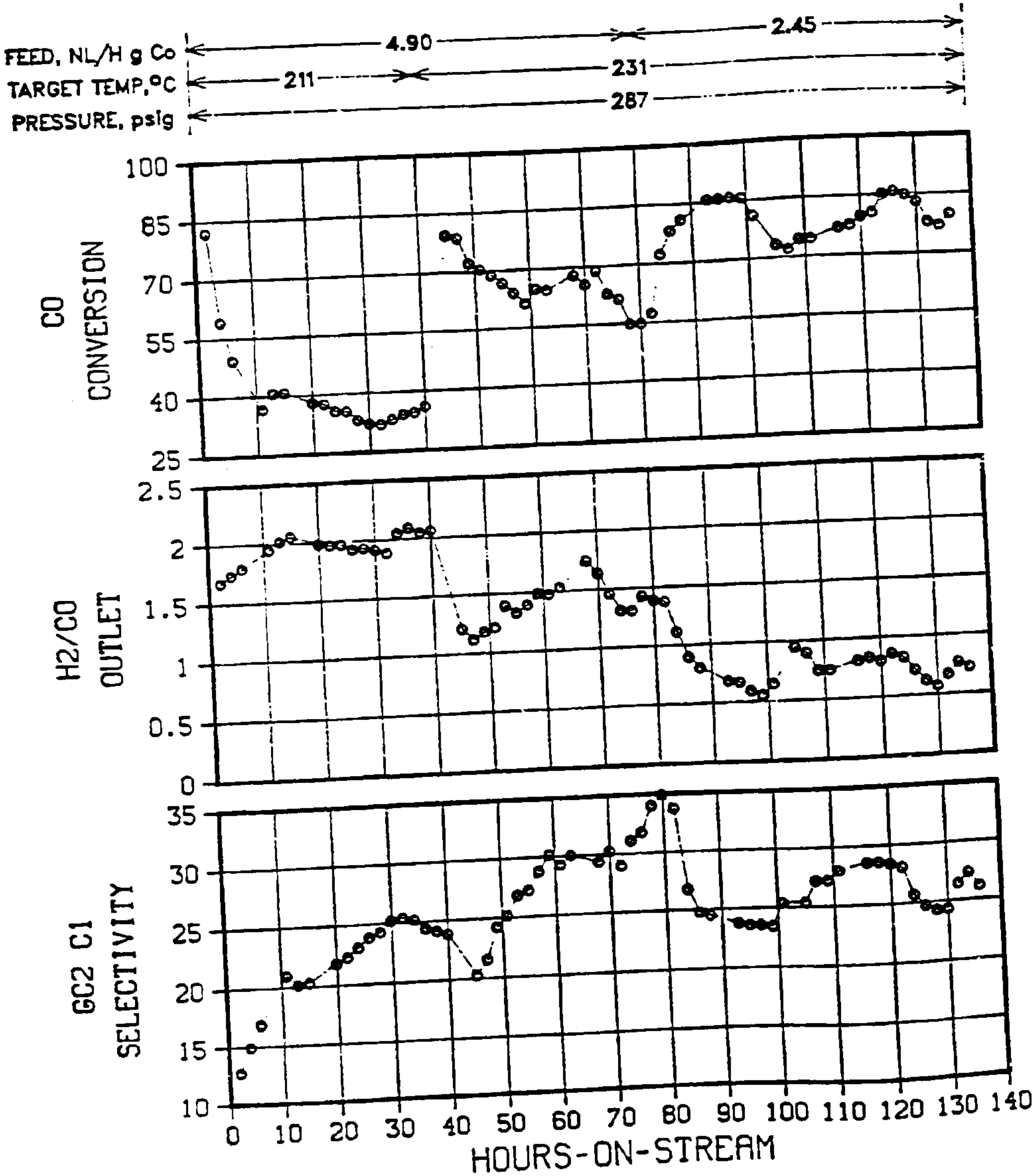


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FIGURE A-4
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

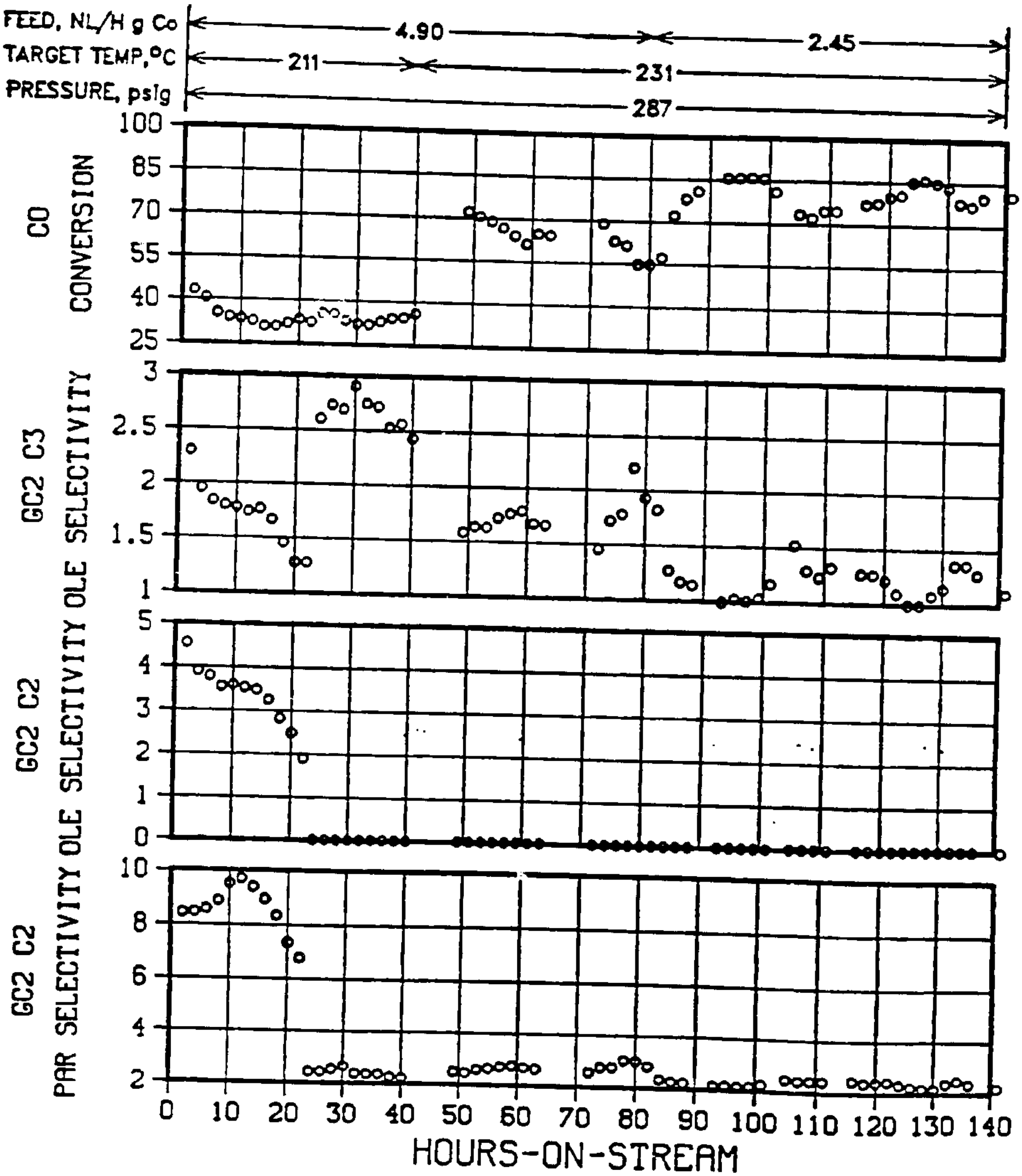

FIGURE A-5
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

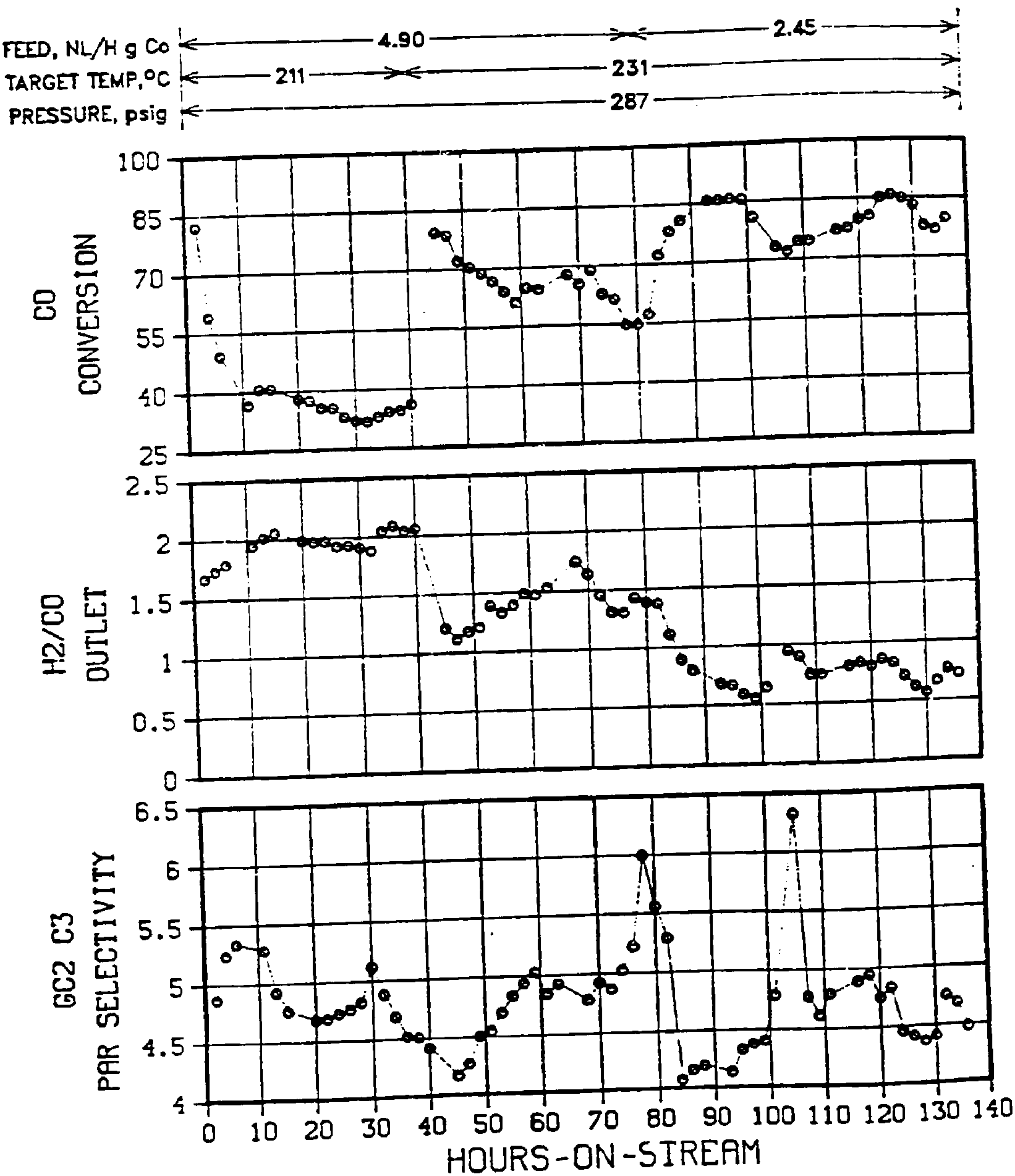

FIGURE A-6
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

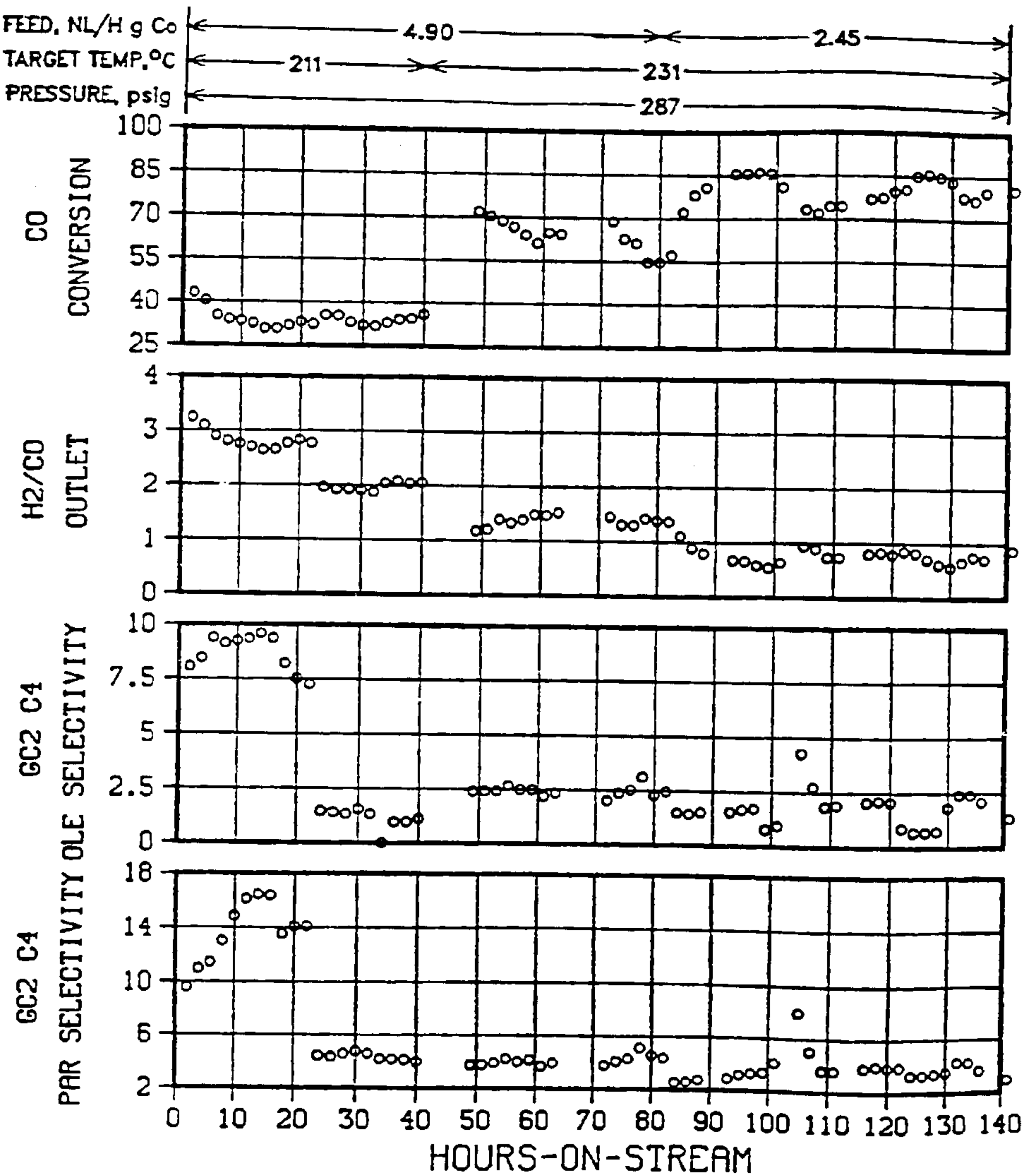

FIGURE A-7
SUMMARY DATA FOR RUN 78 (CATALYST 6531-167)

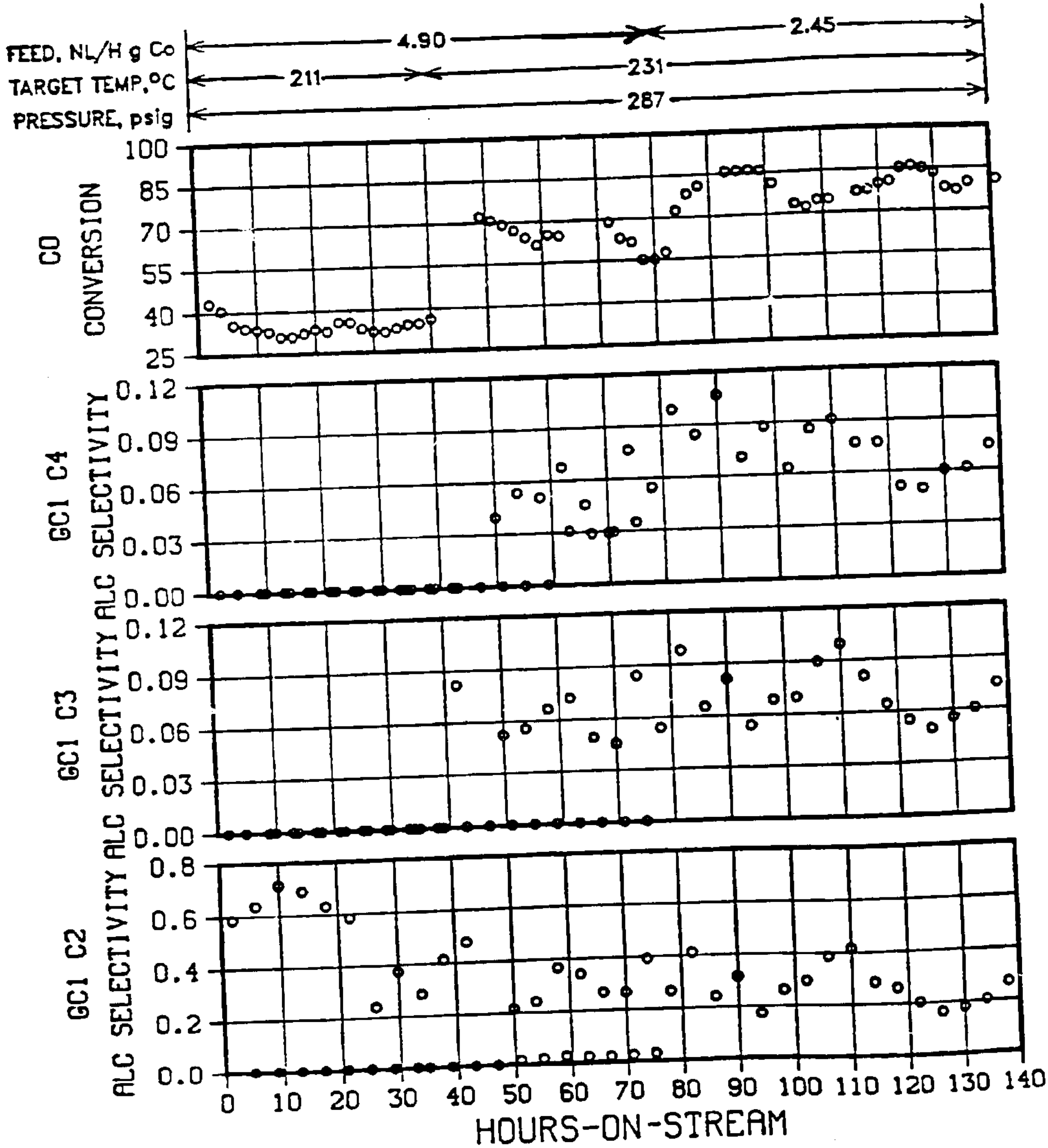

FIGURE A-8
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

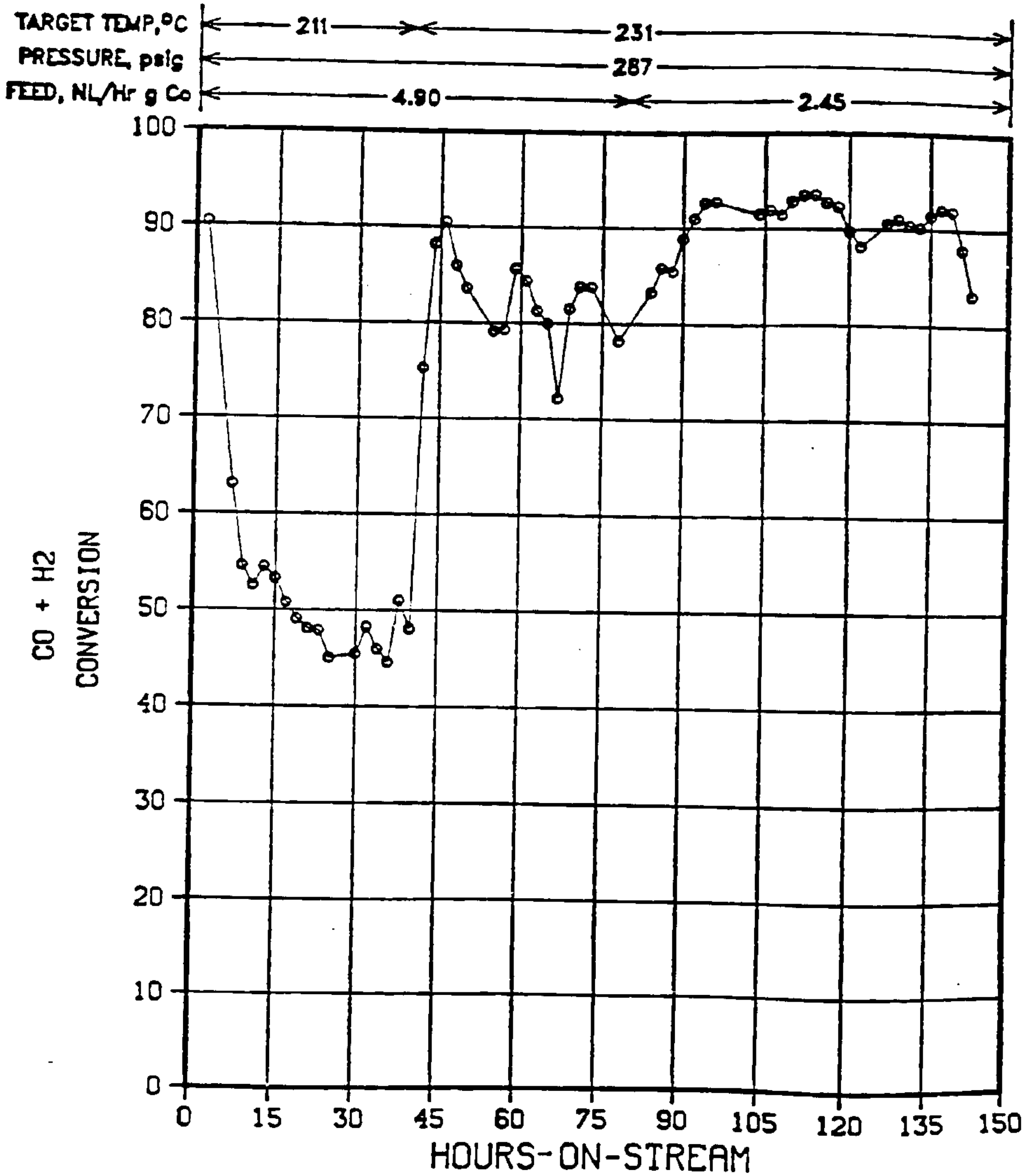

FIGURE A-9
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

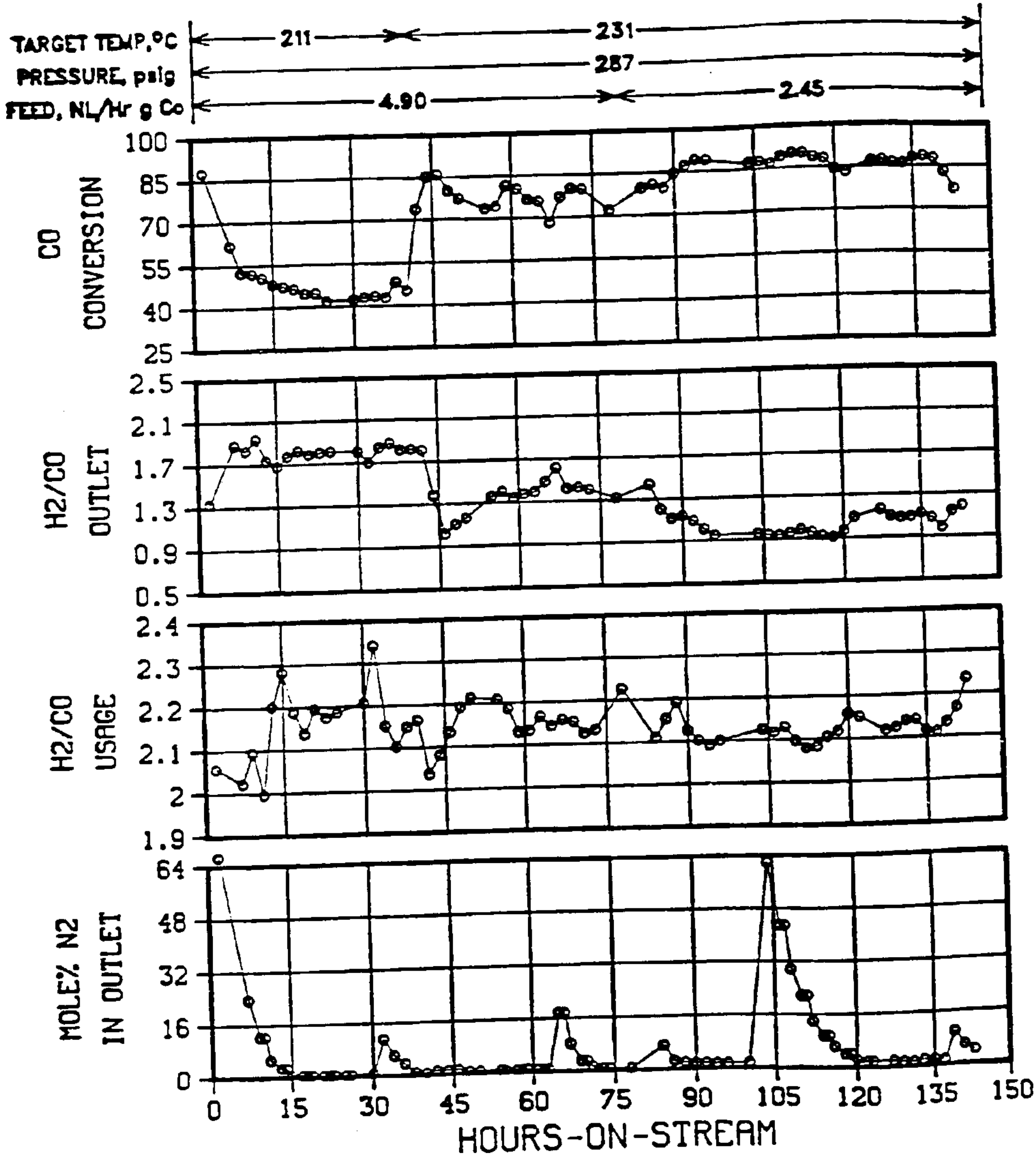

FIGURE A-10
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

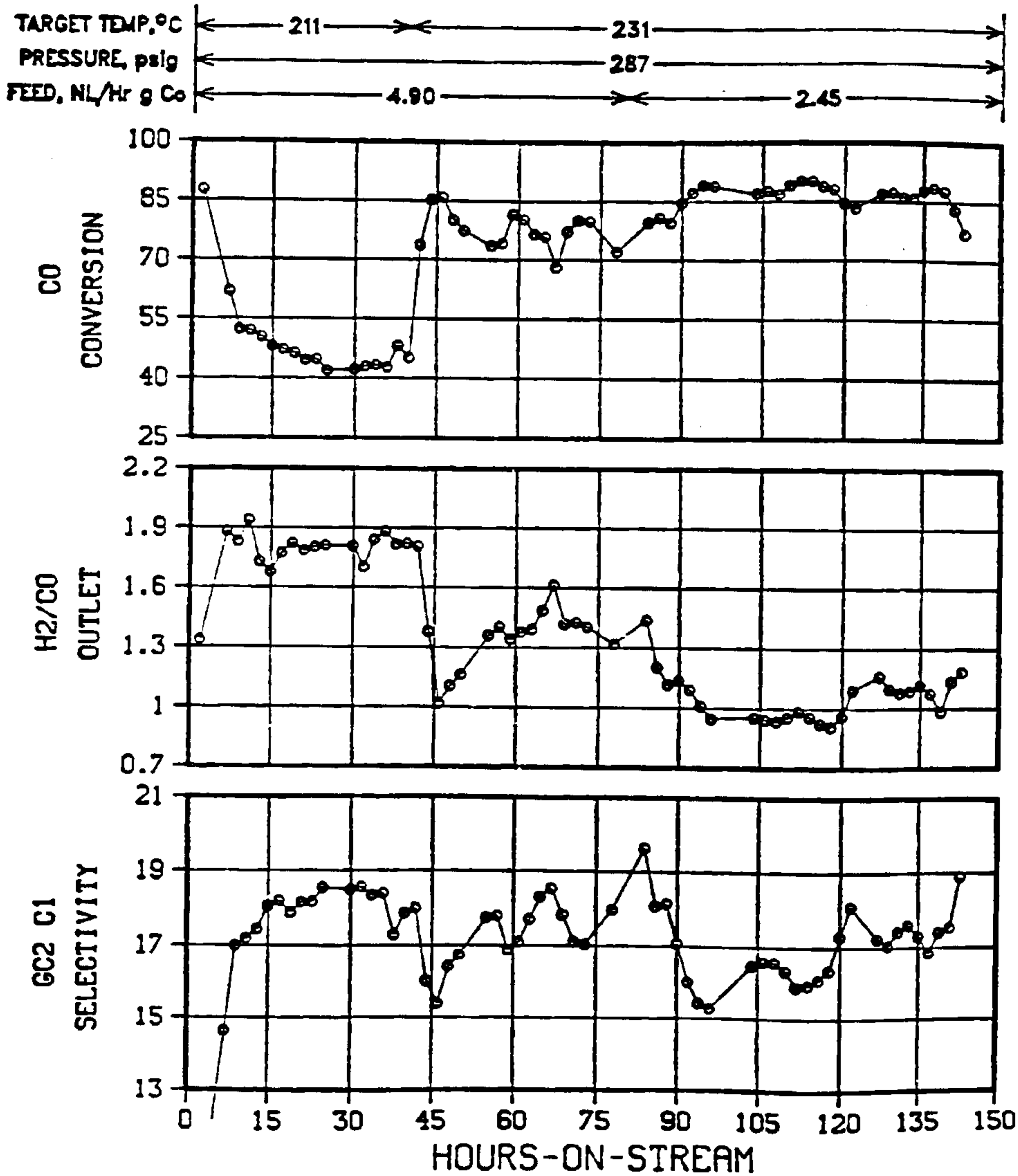

FIGURE A-11
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

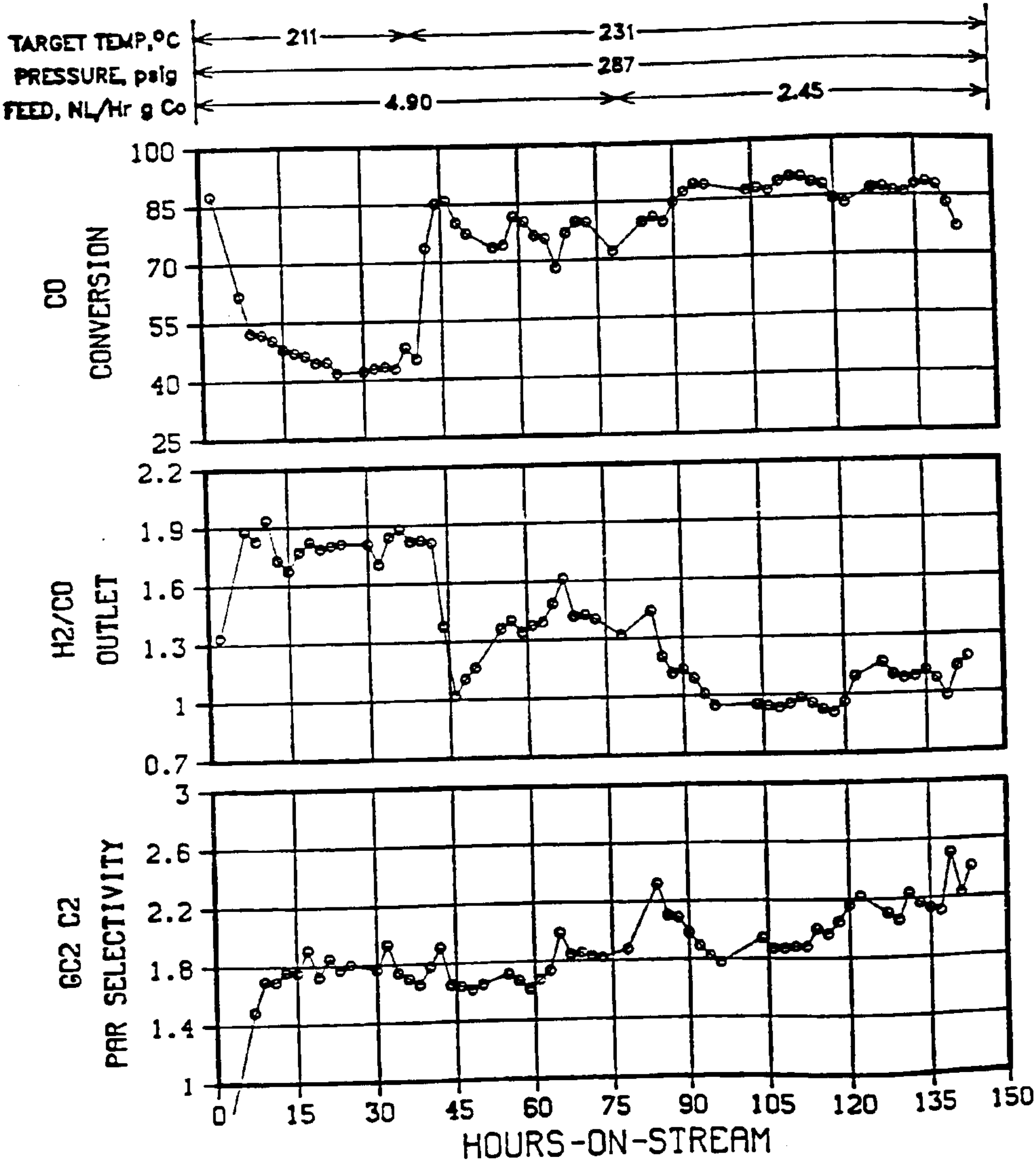

FIGURE A-12
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

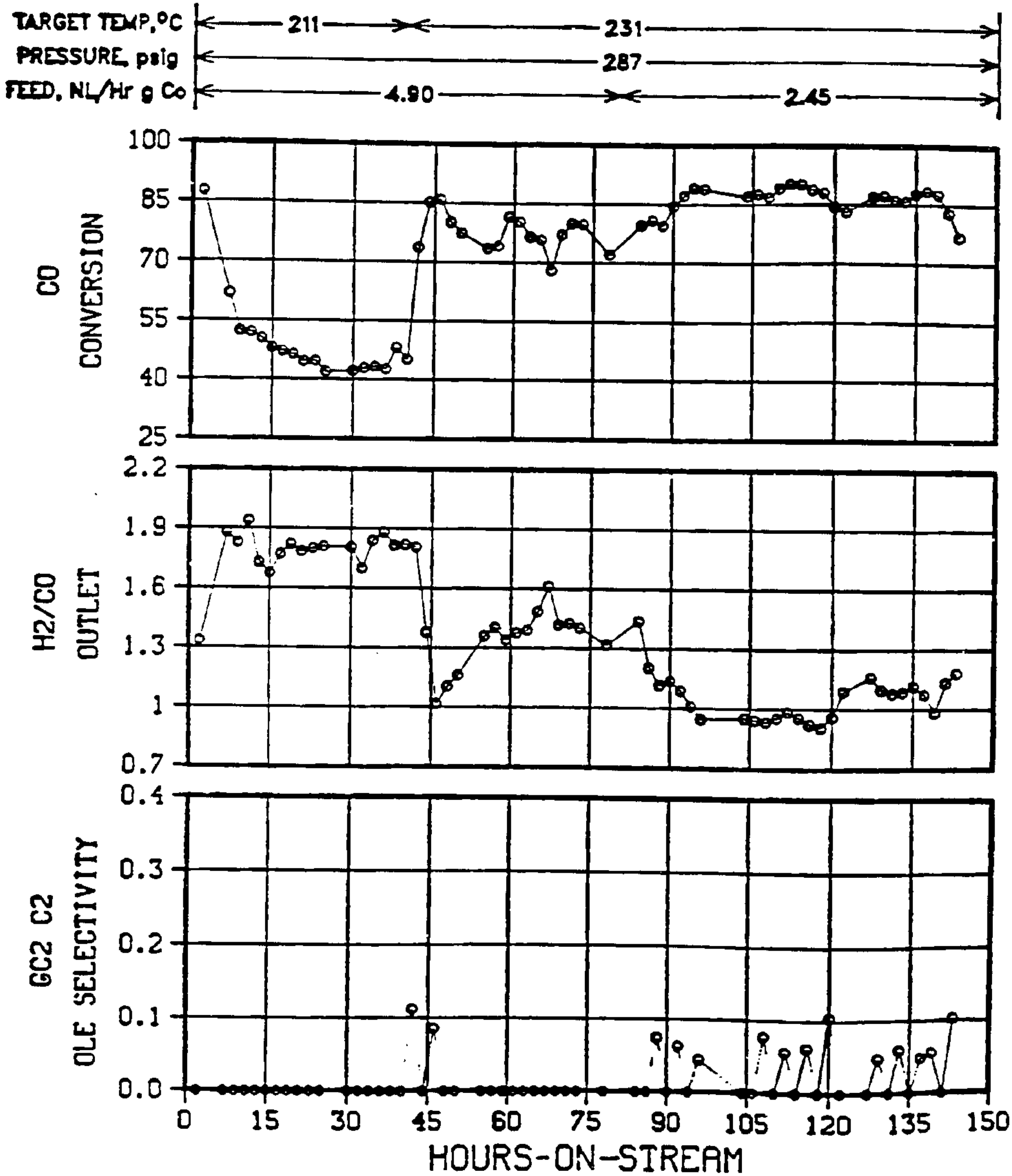

FIGURE A-13
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

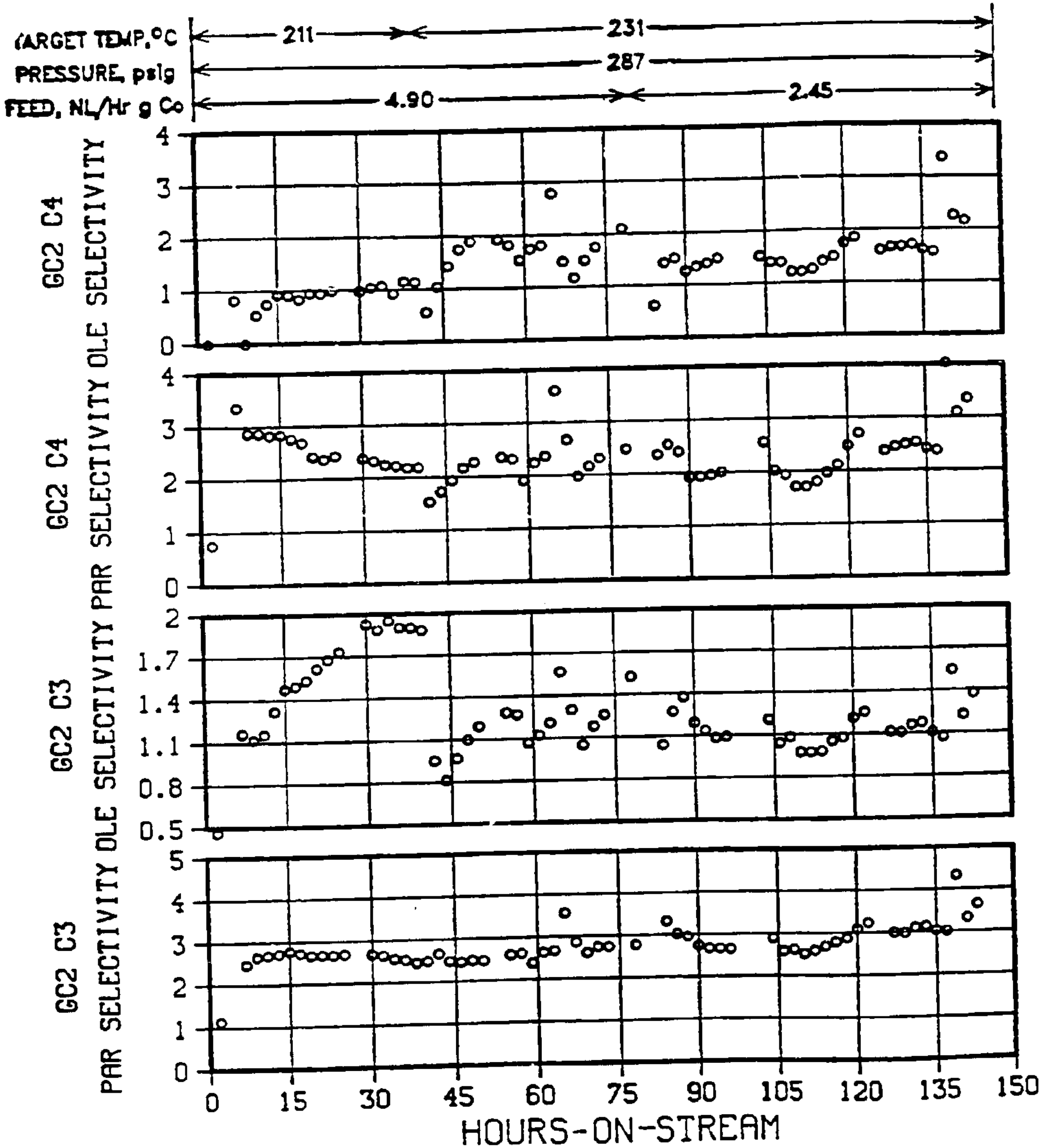

FIGURE A-14
SUMMARY DATA FOR RUN 80 (CATALYST 6531-166)

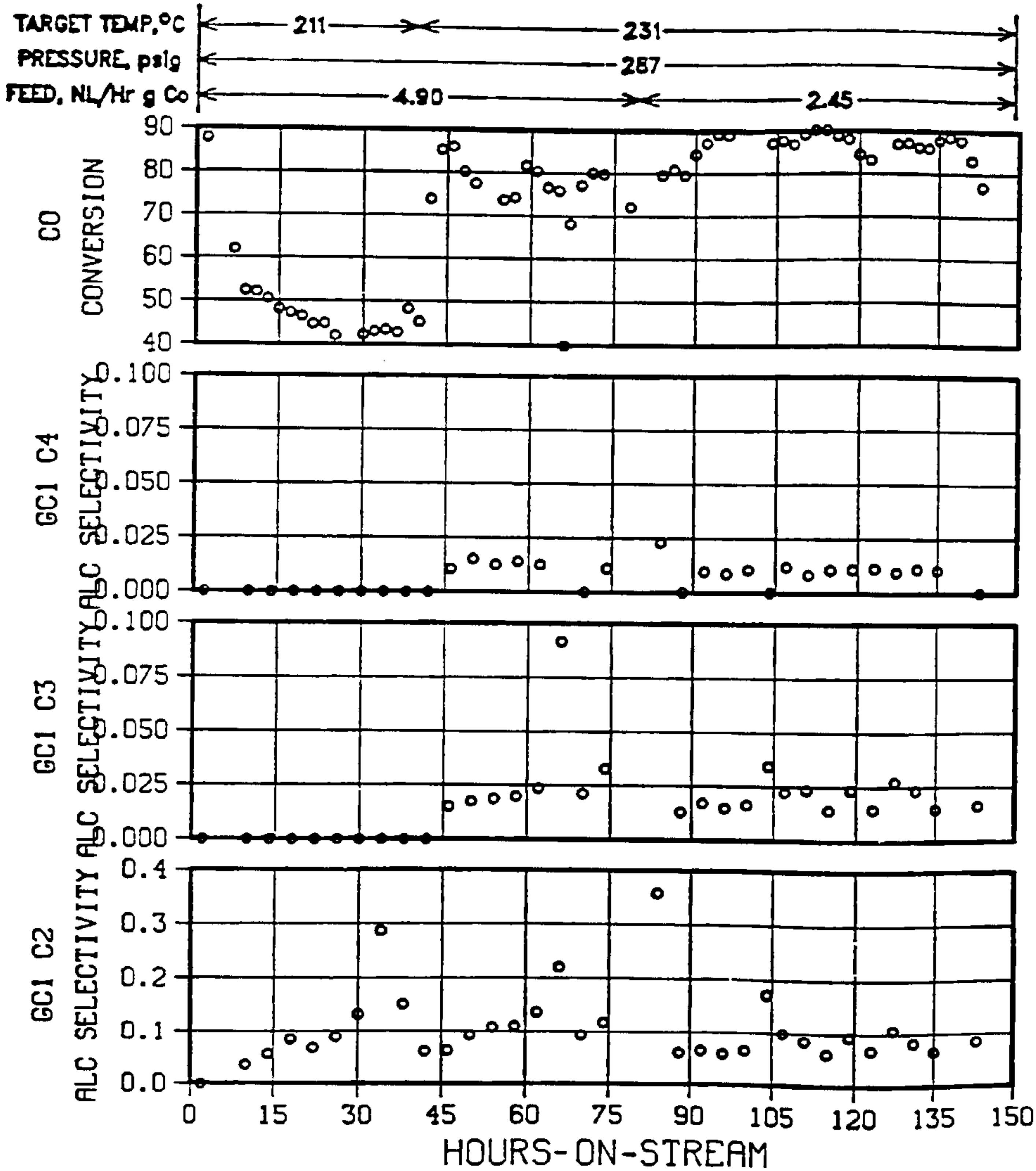

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FIGURE A-15
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

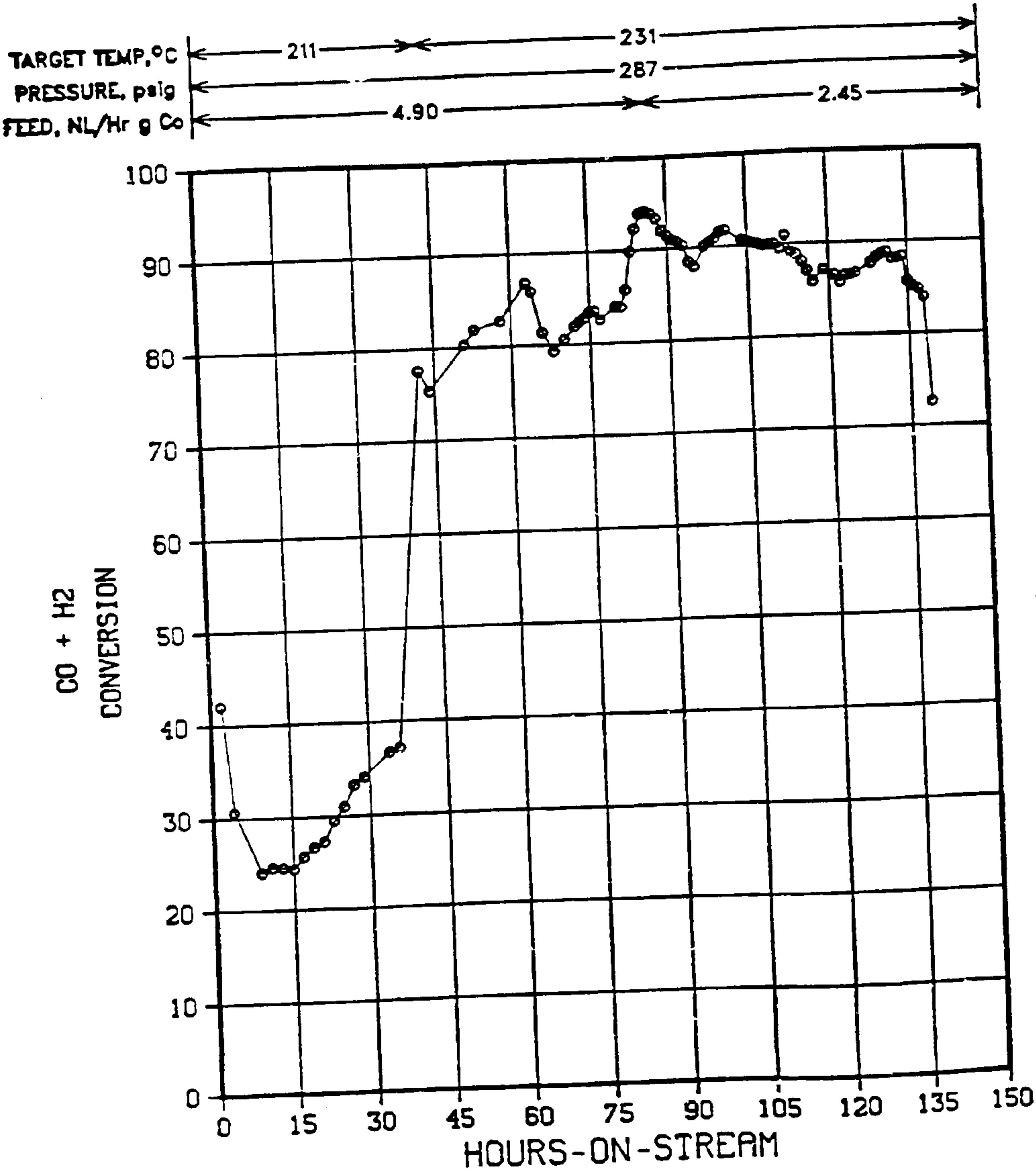

FIGURE A-16
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

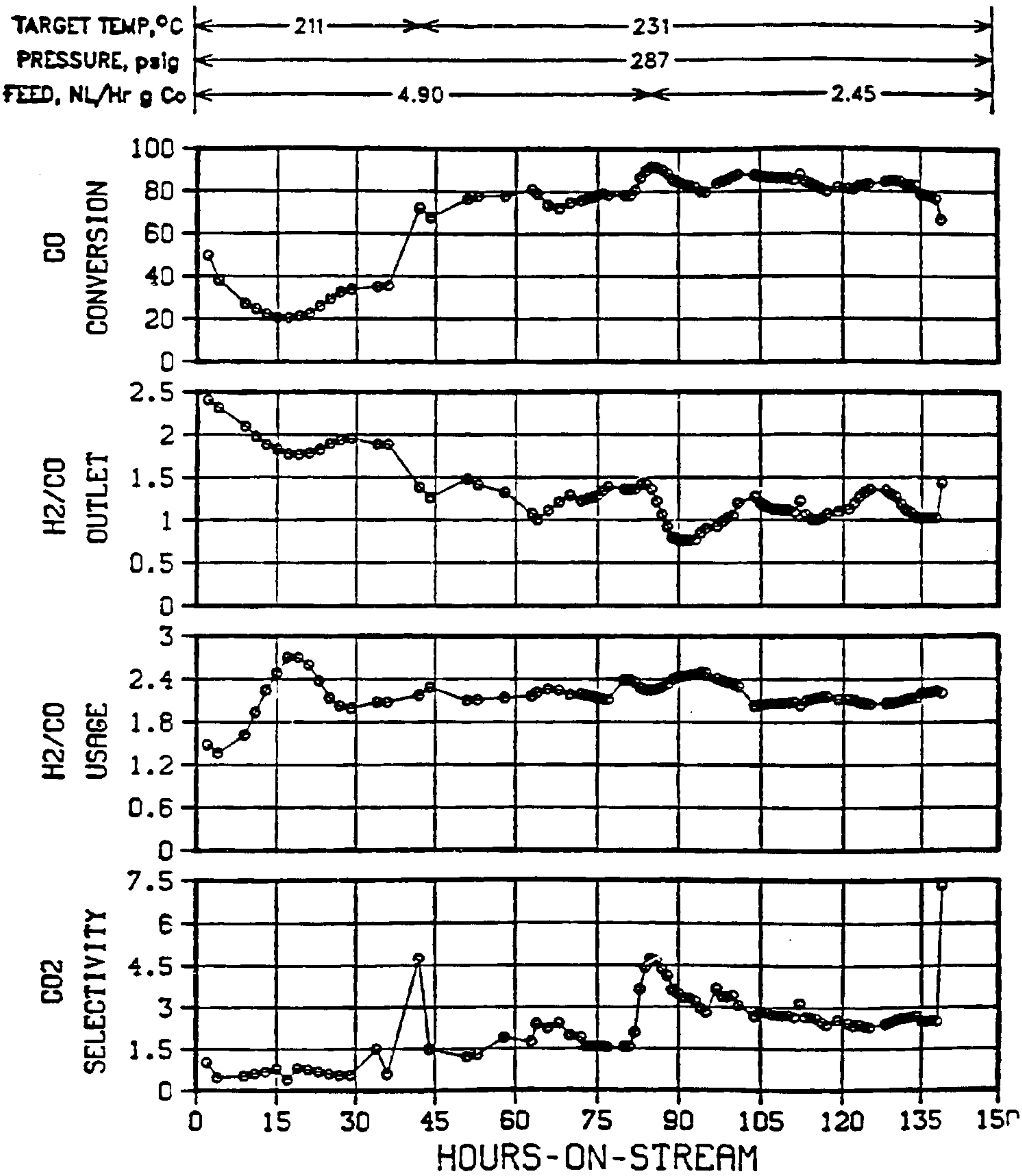

FIGURE A-17
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

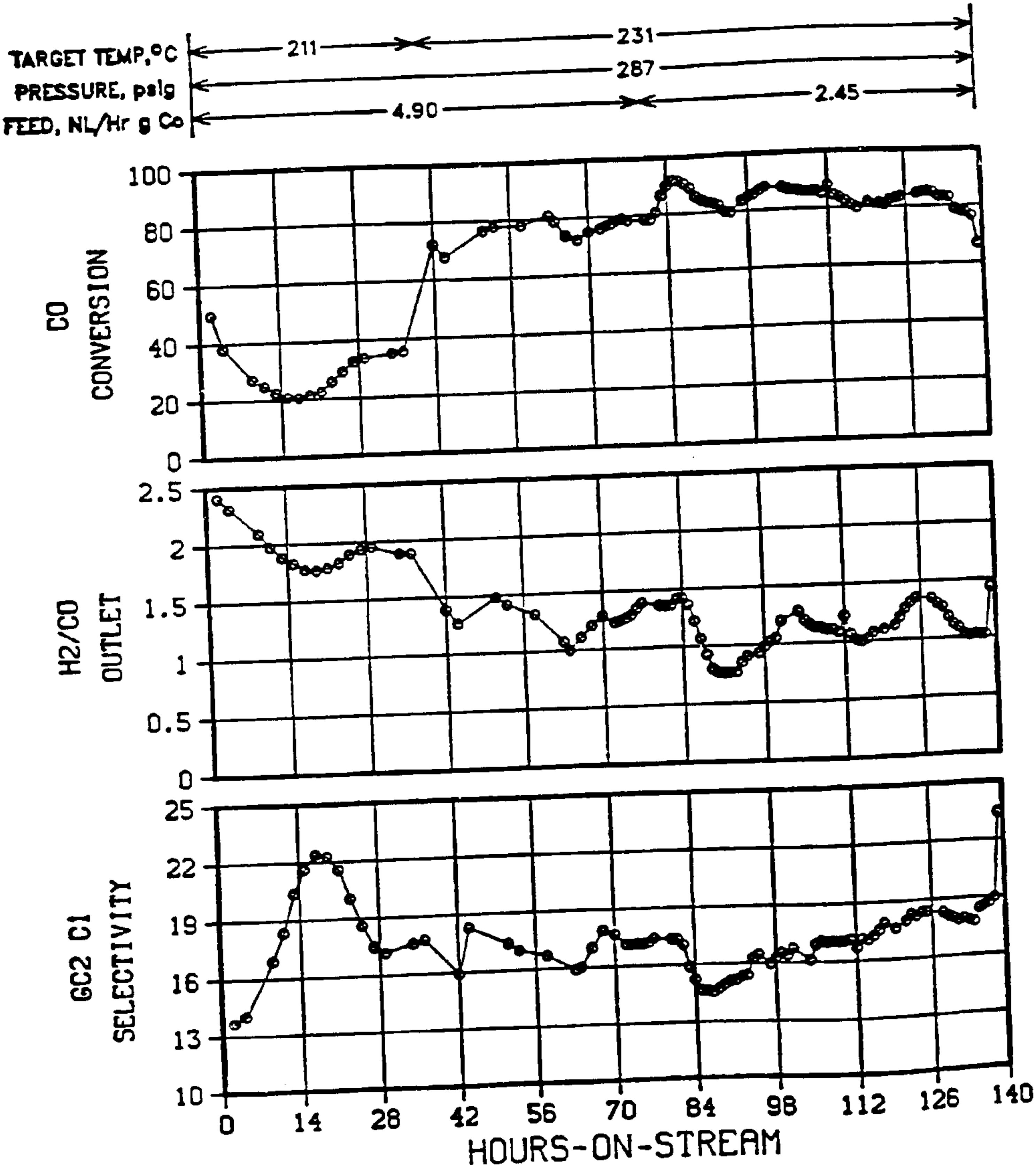

FIGURE A-18
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

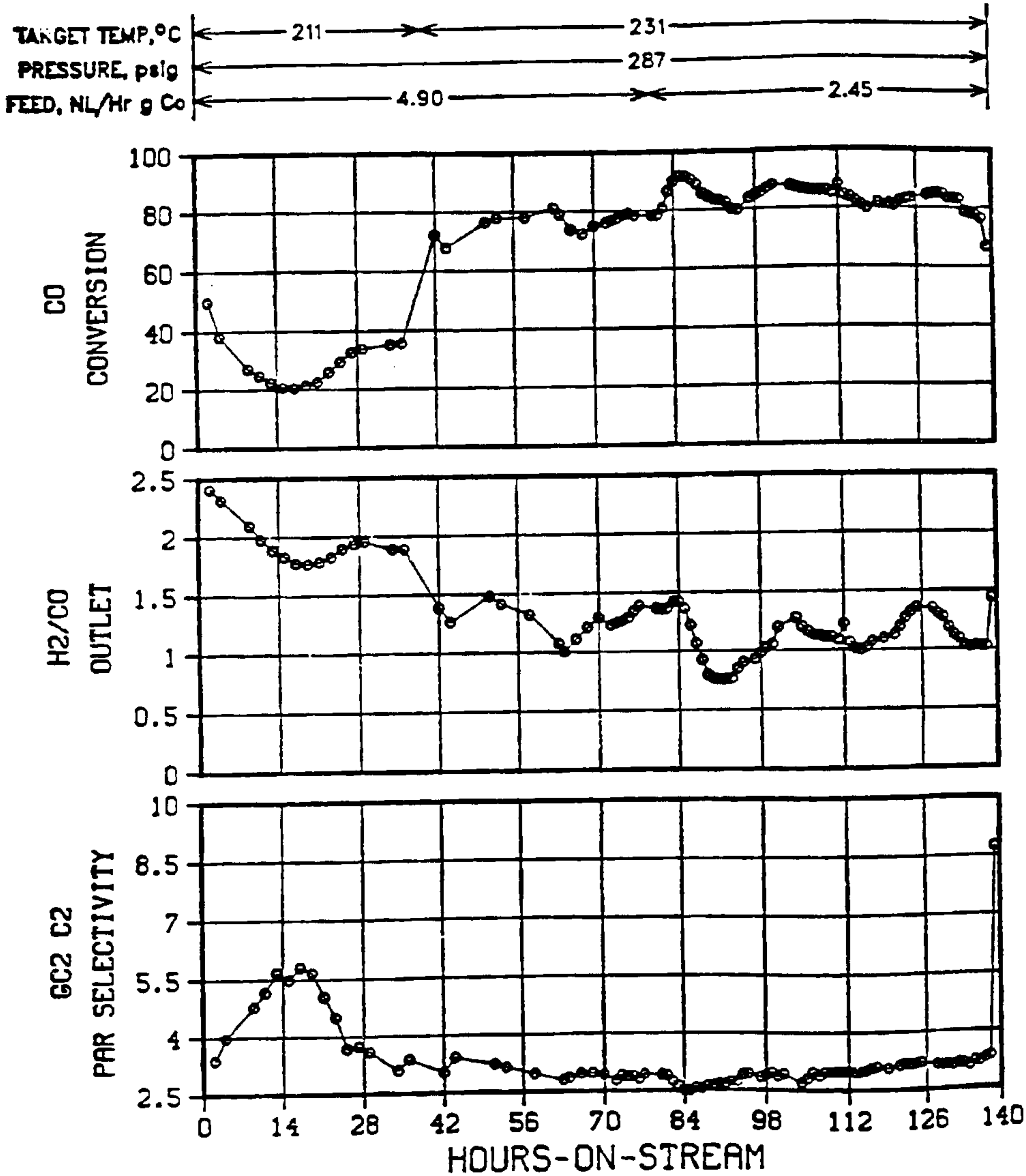

FIGURE A-19
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

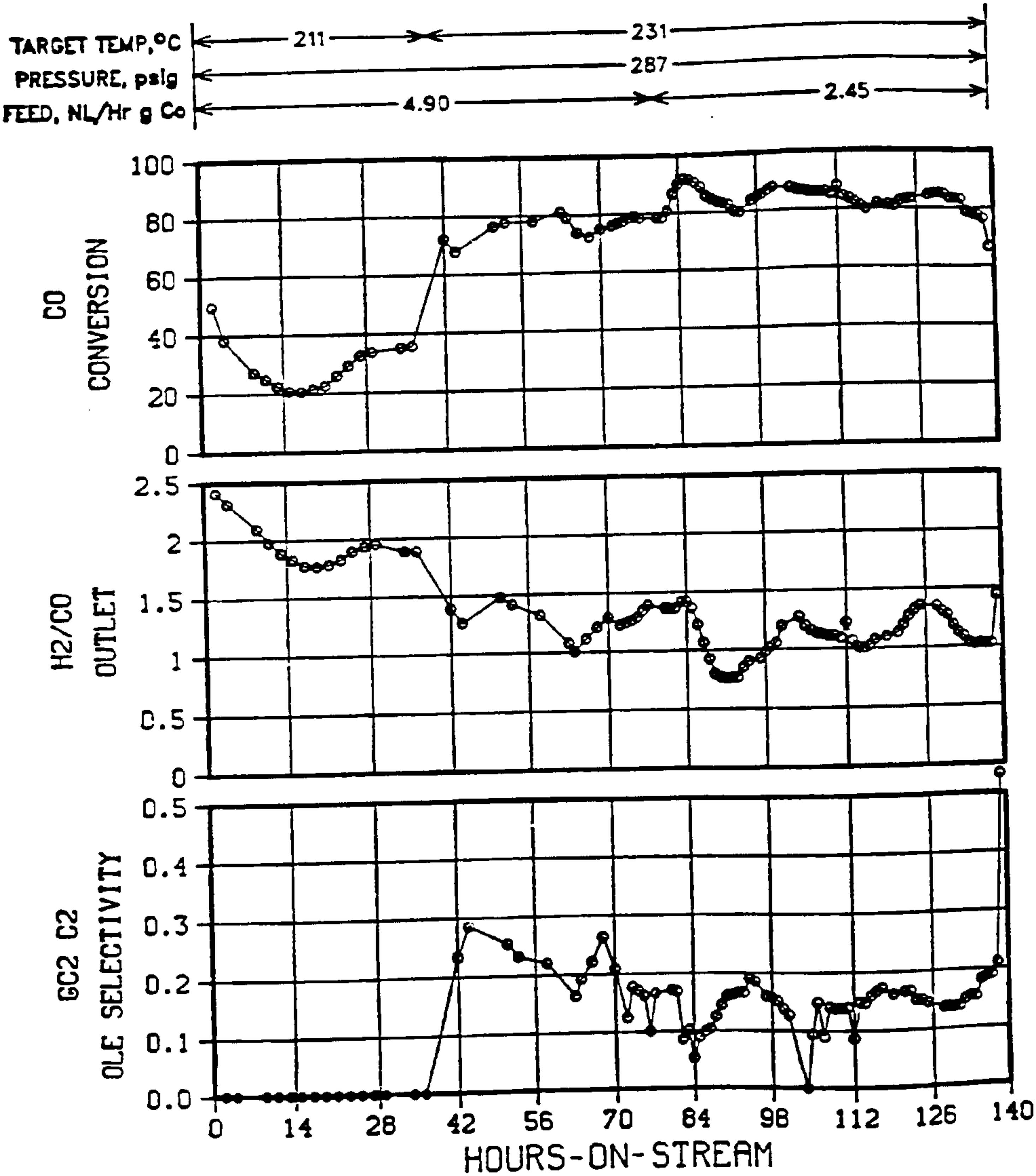

FIGURE A-20
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

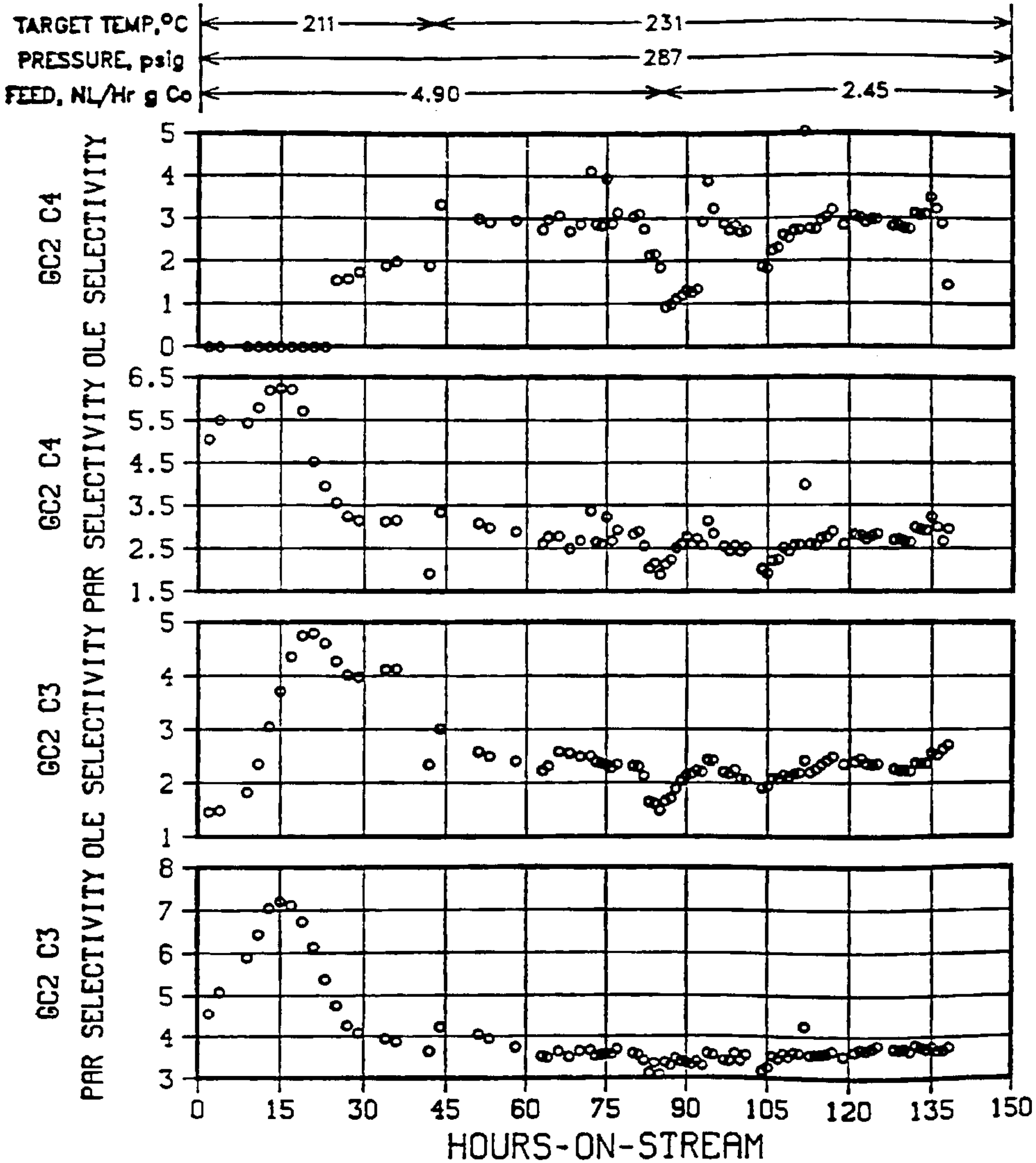

FIGURE A-21
SUMMARY DATA FOR RUN 81 (CATALYST 6531-175)

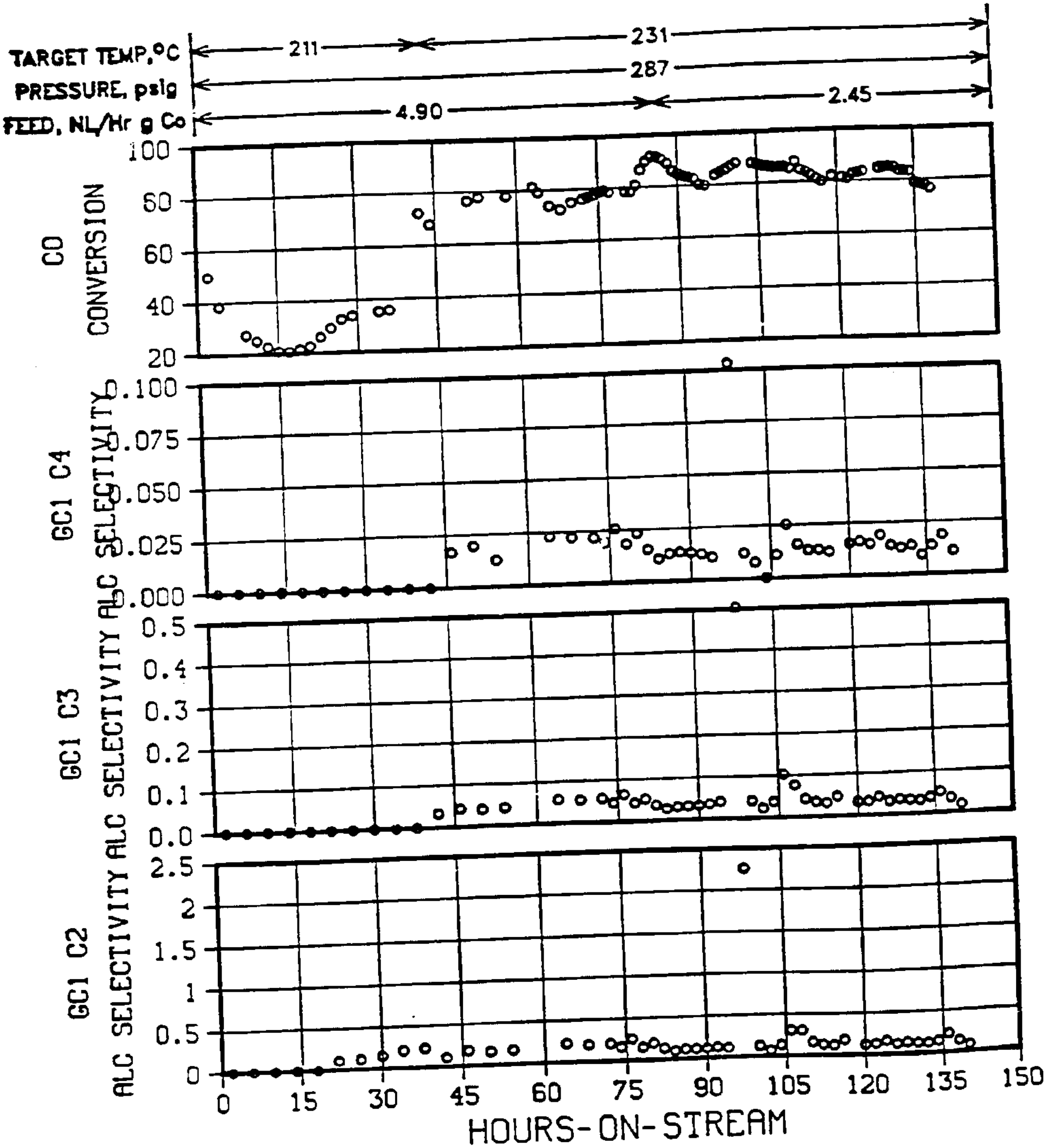

FIGURE A-22
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

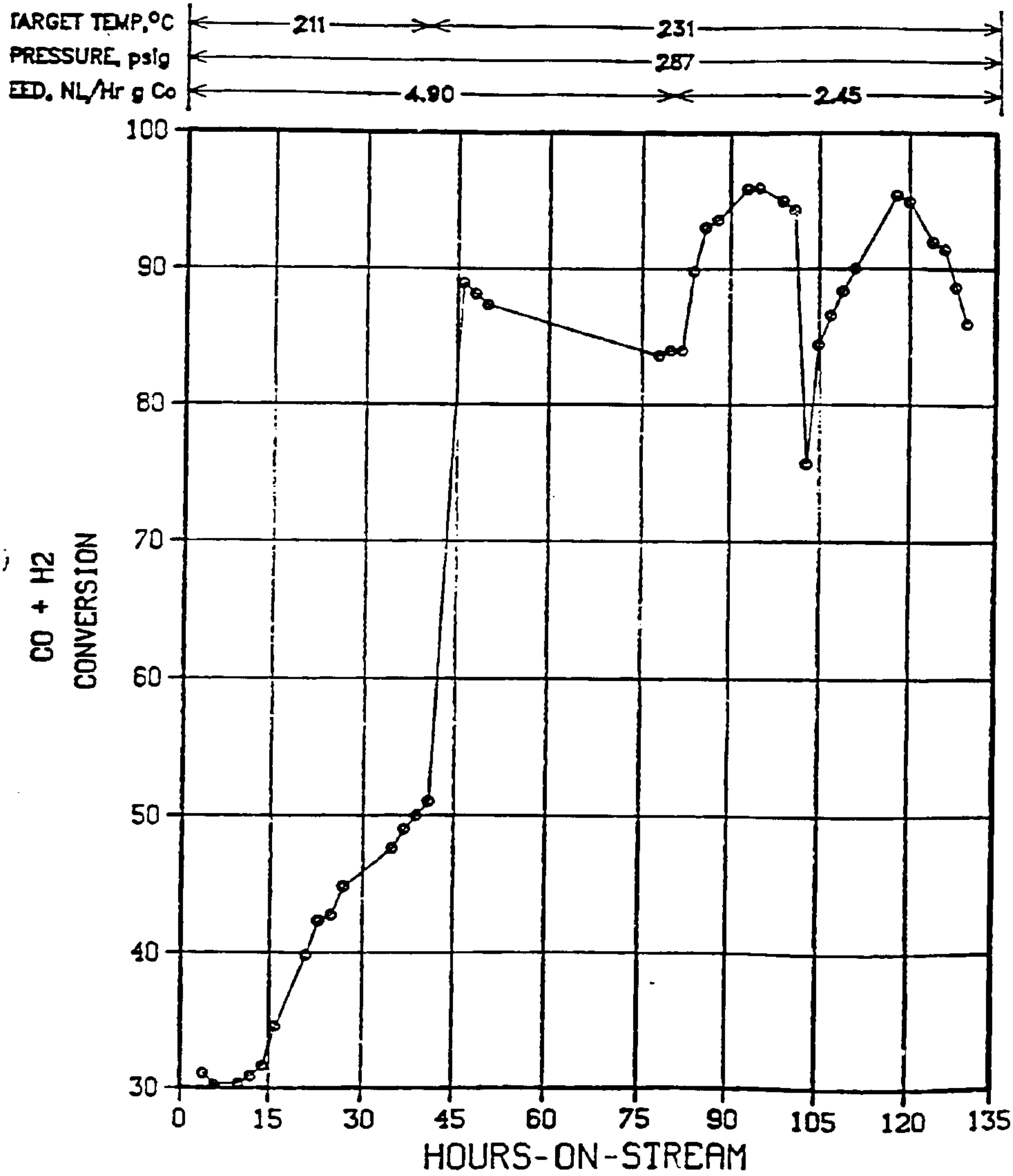

FIGURE A-23
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

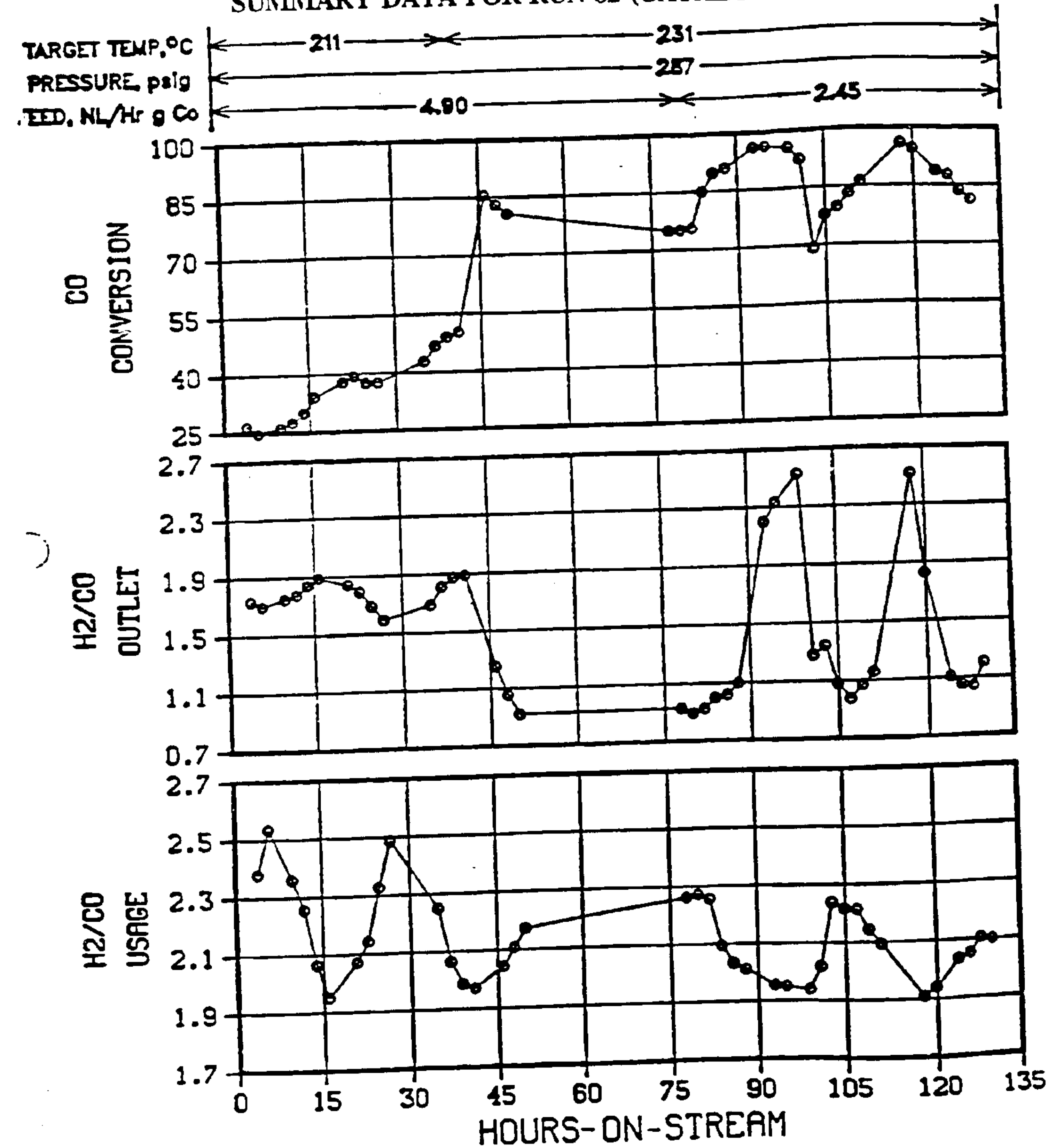

FIGURE A-24
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

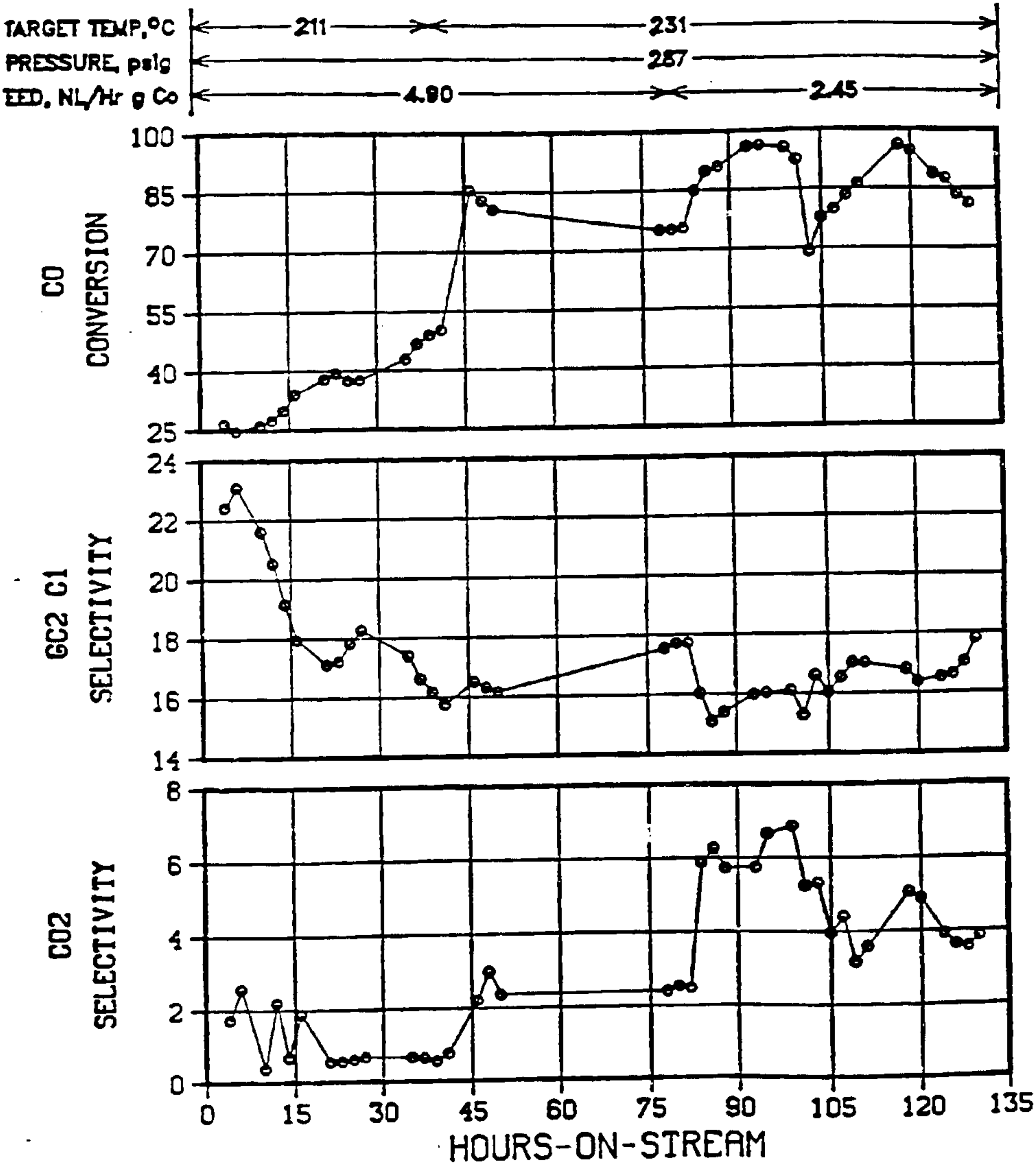

FIGURE A-25
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

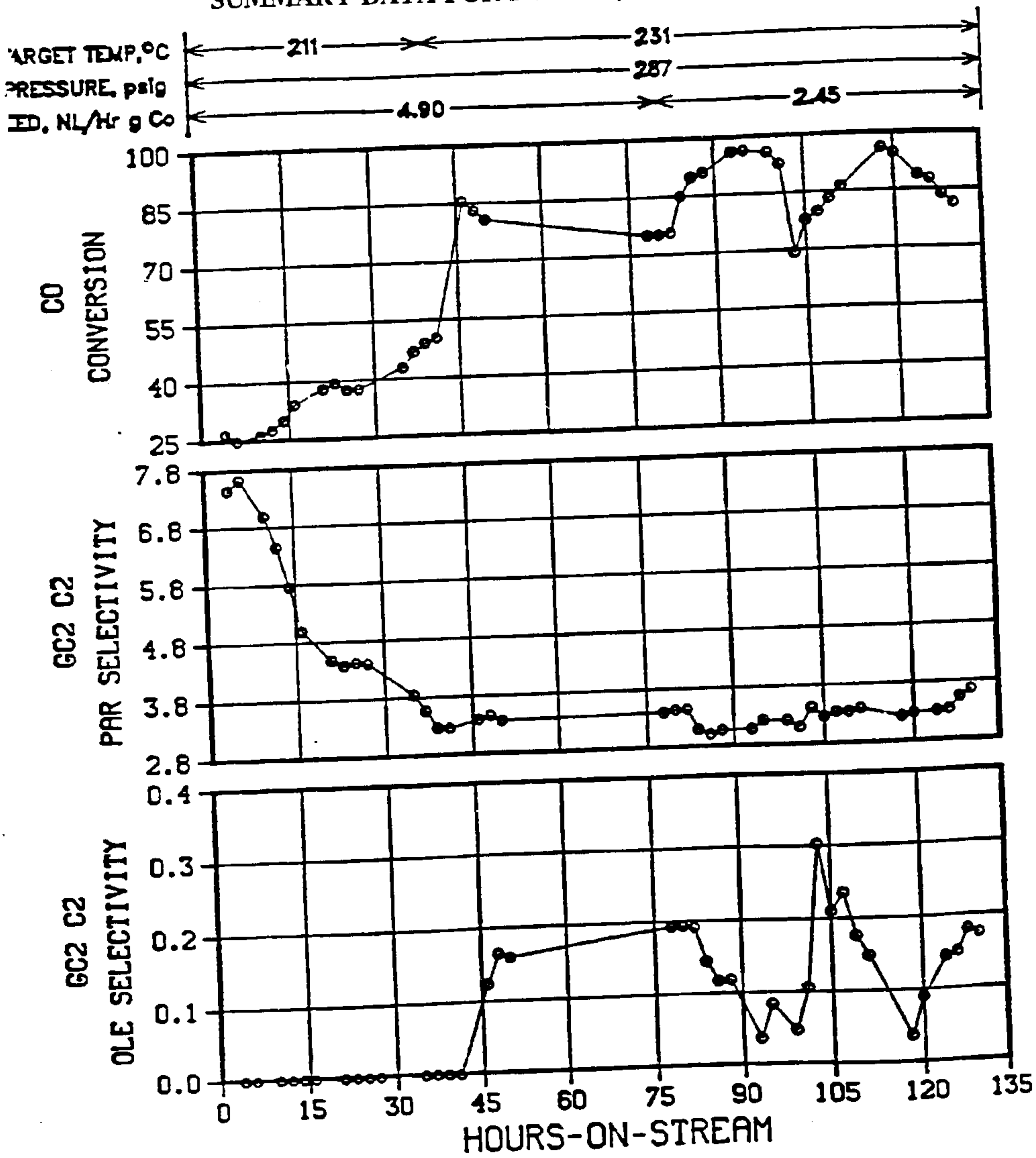

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FIGURE A-26
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

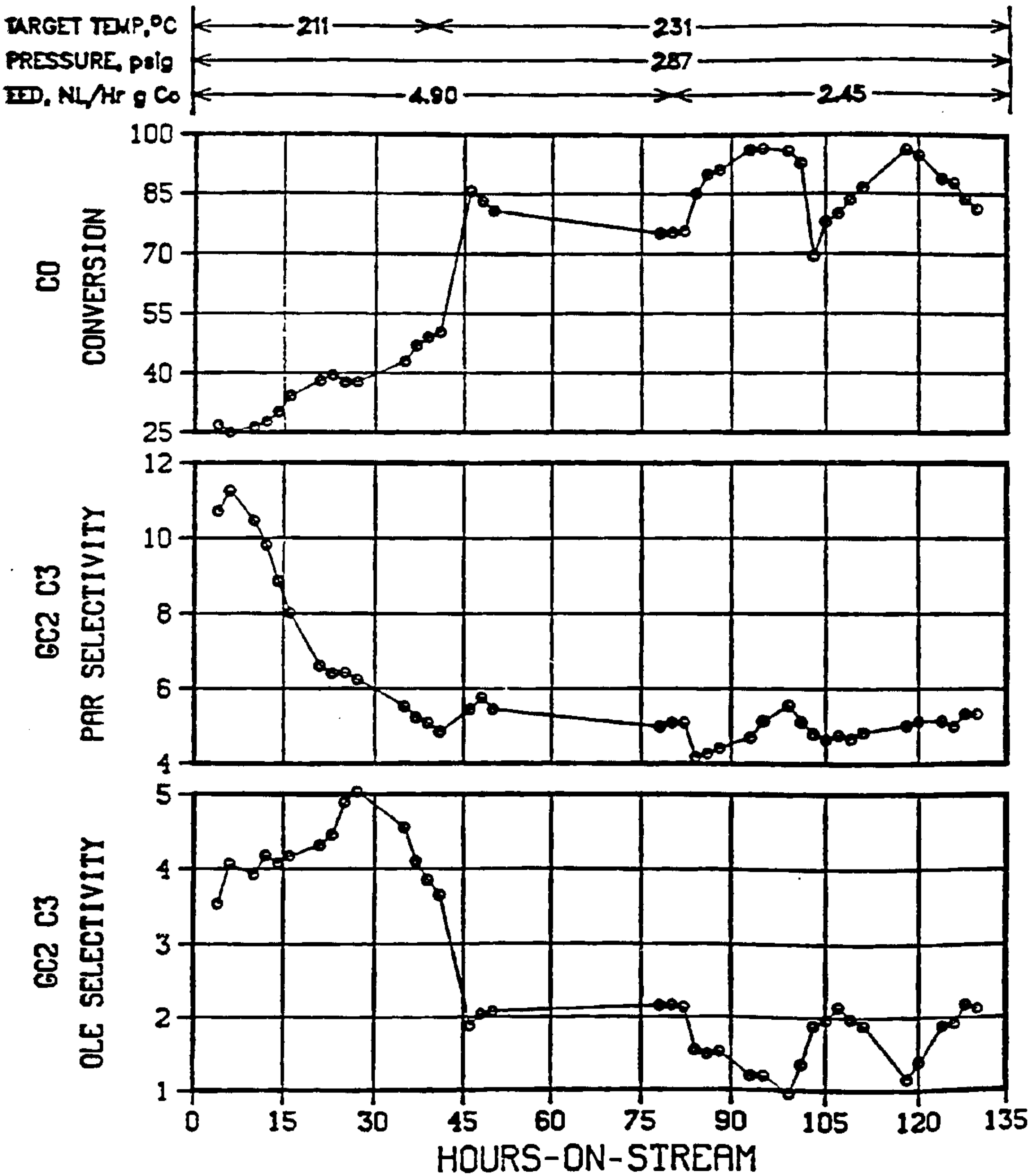

FIGURE A-27
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)

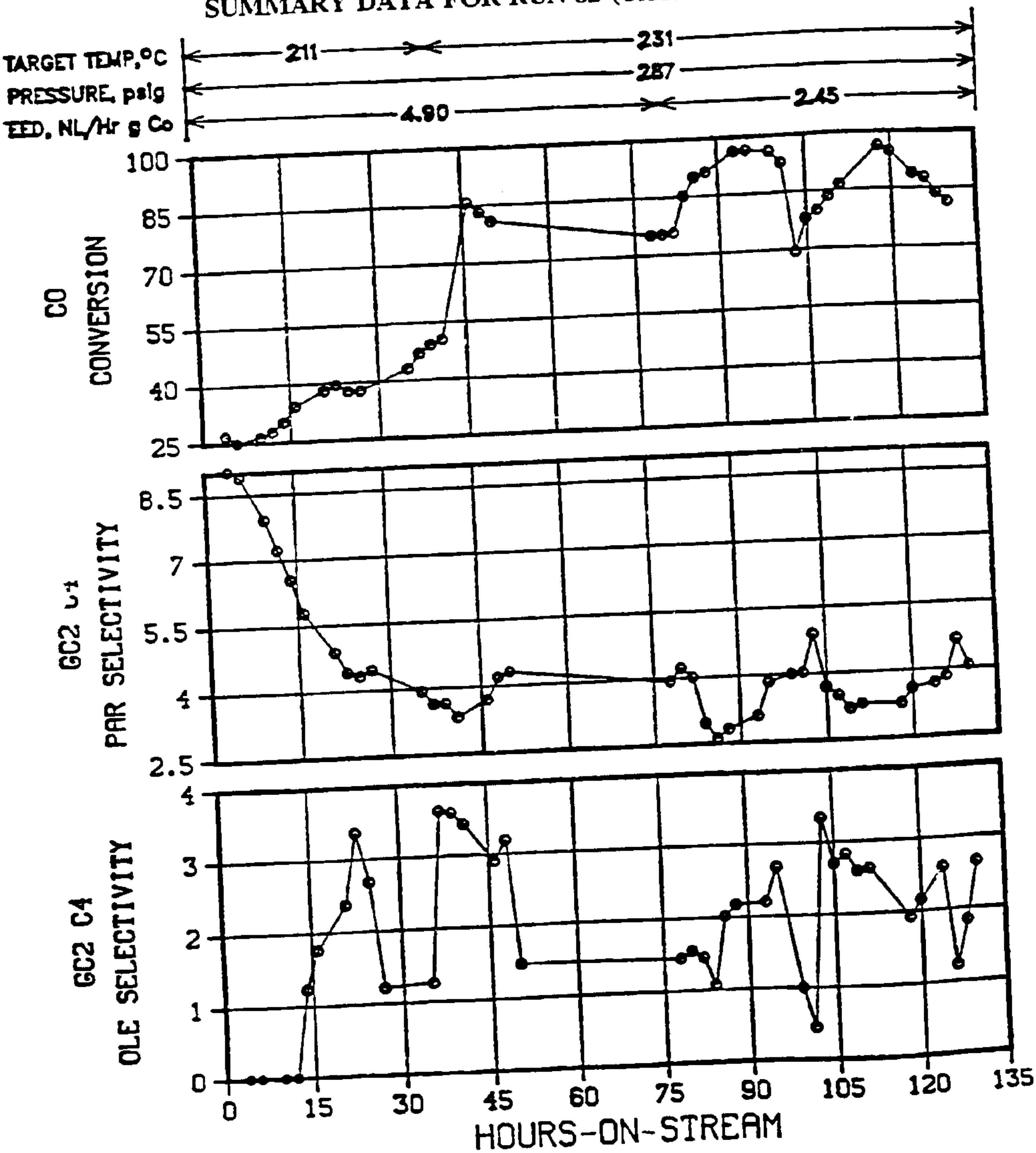

FIGURE A-28
SUMMARY DATA FOR RUN 82 (CATALYST 6531-176)