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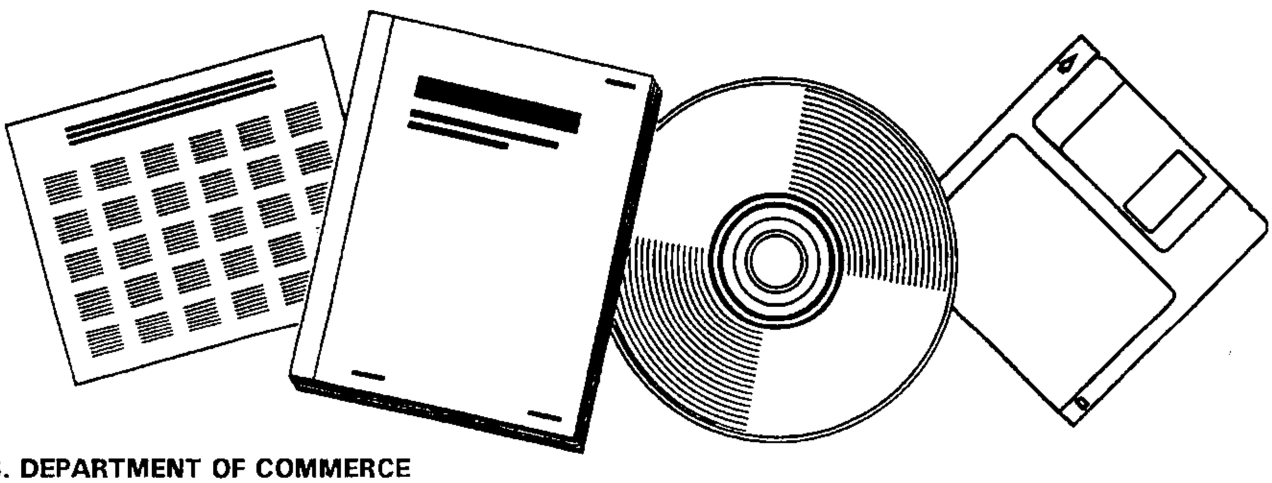
DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST. TECHNICAL PROGRESS REPORT NO. 10, JANUARY 1, 1992--MARCH 31, 1992

UOP, INC.
DES PLAINES, IL

1992



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

DOE/PC/89869--79

DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

Contract DE-AC22-89PC89869

Technical Progress Report No. 10
(1/1/92 - 3/31/92)

by

Robert R. Frame and Hemant B. Gala

UOP
25 E. Algonquin Road
Des Plaines, Illinois

DISCLAIMER

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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.

At the start of an experiment, 13 g of catalyst (>40 mesh in size) is loaded in the fixed-bed reactor with 160 g of diluent. In most runs quartz sand (60 to 80 mesh in size) is used as the diluent. For runs 63 and 67, α-alumina (40 to 80 mesh in size) was used as the diluent. Catalyst 585R2796 (Run 67) and 305R0160 (Run 77), prepared on carbotrap B support were 170 to 325 mesh in size. The diluent is used because of the very exothermic nature of the Fischer-Tropsch reactions. 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 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 lower at higher conversion. One goal of the current work is to develop high activity catalysts which exhibit low methane selectivity. All the catalysts evaluated with the exception of the reference catalyst contained ruthenium. A few also contained manganese and zirconium which were also on the reference catalyst (Table 2).

For runs discussed in this report, the run summary plots of conversions and selectivities as a function of hours-on-stream are attached. From these plots data were abstracted to prepare tabular summaries which allow comparison of catalyst performance (Tables 3 and 4).

Scope of Work During Reporting Period

Screening of experimental catalysts continued during this quarter. The reference catalyst, TC 211, was prepared under an earlier Union Carbide contract with the DOE (DOE-AC22-84PC70028) and consists of cobalt, manganese and zirconium deposited on a special Y zeolite-derived support. It exhibits good activity and low methane selectivity (Table 3 and 4). During that contract, this catalyst was found to be very stable.

The initial goal of this project is to identify suitable support materials for cobalt-ruthenium based Fischer-Tropsch catalysts. As reported in the previous two quarterly reports, several promising materials have emerged: magnesium oxide, 50/50 alumina/titania, and carbon. All are very pure; in particular, free of sulfur.

In this quarter, additional catalysts that were supported on these three promising materials were evaluated. The STEM apparatus was inoperable for most of this time period, thus only a minimal amount of catalyst characterization was done.

Results and Discussion

Runs 63, 69 and 72

These three runs employed magnesium oxide-supported catalysts. Runs 63 (catalyst 585R2757) and 69 (catalyst 585R2810) were discussed in previous reports from this project (Reports 7-9 covering the period of April to December, 1991). The hourly run summary data for Run 72 (catalyst 305R0142) are in Appendix A, Figures 1-8.

None of the catalysts supported on magnesium oxide were as active as the reference TC 211 catalyst at condition 1. At Condition 3 in Run 69 the conversion was close to the reference catalyst at Condition 1; the methane selectivity was 11.1% compared to 7.0% for the reference catalyst. Although these catalysts exhibited the lowest methane selectivities of all the experimental catalysts herein, they were still more methane selective than the reference catalyst. All of the catalysts were more selective to alcohols than the reference catalyst (Table 4). The reverse micelle impregnation method did not appear to be much less selective to methane than a similar catalyst prepared by an aqueous impregnation (Run 63 vs Run 72). There was at best a slight activity advantage for the reverse micelle catalyst.

Runs 68 and 73

These two runs used catalysts prepared on 50/50 alumina/titania. Run 68 (catalyst 585R2775) was discussed in a previous technical progress report from this project (Report No. 9 covering the period October to December, 1991). The hourly run summary data for Run 73 (catalyst 305R0134) are in Appendix A, Figures 9-16.

The alumina/titania-supported catalysts both produced high levels of methane. There did not seem to be an advantage to the reverse micelle catalyst preparation route from the standpoint of either activity or selectivity at Condition 1. At Condition 2 the reverse micelle catalyst was more active and less selective for methane than the aqueous catalyst. These two catalysts also were more selective to alcohols than the reference catalyst. The alumina/titania catalysts seemed to be slightly more active than the magnesium oxide ones at Condition 1.

Runs 67 and 77

These two runs used catalysts supported on Carbotrap B which is a high purity, fine mesh carbon. Run 67 (catalyst 585R2796) was discussed in previous technical reports of this project (Reports 7 and 8 covering the period July to September, 1991). The hourly run summary data for Run 77 (catalyst 305R0160) are in Appendix A, Figures 17-24.

Catalyst 305R0160 (Run 77) was the most active of the experimental catalysts screened for this report, in spite of this it was not as active as the reference catalyst. These catalysts also exhibited high selectivity to methane at all test conditions. Catalyst 305R0160 was the only one of the experimental catalysts which exhibited the low alcohol selectivity of the reference catalyst. Comparison of runs 67 and 77 indicate that reverse micelle impregnation of Carbotrap B did not produce a catalyst that is less selective to methane at condition 1 than simple aqueous impregnation.

Summary and Implications for Further Work

In this report and the three before it progress has been reviewed toward finding a support for cobalt/ruthenium-based Fischer-Tropsch catalysts. Of the support materials investigated three have so far shown promise: magnesium oxide, carbon and 50/50 alumina/titania. However, as yet catalysts supported on these three materials have proven inferior to the reference TC 211 Y zeolite-supported catalyst with regard to both activity and selectivity. Ruthenium is considered to be a promoter of activity, however, if this effect is manifested in the experimental catalysts it is not enough to make the catalysts more active than the ruthenium free reference catalyst. The advantages due to reverse micelle are, so far, minimal at best.

When the experimental catalysts were operated at higher conversions through evaluation at Conditions 2 and 3, the magnesium oxide-supported catalysts appeared to be closest to the desired low methane selectivity of the reference catalyst at similar conversion.

The catalysts prepared on the above supports were not superior to the reference catalyst TC 211. Since the main objective of the current contract is to determine whether cobalt/ruthenium catalysts can be prepared which are superior to cobalt only catalysts, the Y zeolite support will be used in the future. In this special Y zeolite-derived support crystallite size is controlled by the pore size distribution. Thus, the catalyst development objective of controlling the crystallite size will be achieved.

In the following quarters, work carried out on the cobalt and cobalt/ruthenium catalysts supported on the Y zeolite-derived support will be reported.

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
Composition of Catalyst Precursors
by Atomic Absorption Spectroscopy and Stem

Run No.	Catalyst No.	Support	AAS, wt-%	Crystallites Size, A	Element. Anal., wt-%
65	TC 211	Steamed, acid-washed Y zeolite	Co, 8.3; Mn, 1.3; Zr, 1.0	50-100	Co, 19.9; Mn, 3.7; Zr, 3.7
63	585R2757[1]	Ultra pure MgO	Co, 7.3; Mn, 0.61; Zr, 0.93; Ru, 1.2		
69	585R2810[2]	Ultra pure MgO	Co, 8.0; Ru, 0.84	100-200	Co, 14.4; Ru, 1.0
72	305R0142[2]	Ultra pure MgO	Co, 7.5; Mn, 0.60; Zr, 0.90; Ru, 0.17		
68	585R2775[1]	Al_2O_3/TiO_2 50/50	Co, 2.7; Ru, 0.49		
73	305R0134[2]	Al_2O_3/TiO_2 50/50	Co, 7.5; Ru, 0.3		
67	585R2796[1]	Carbotrap B	Co, 5.8; Ru, 1.0		
77	305R0160[2]	Carbotrap B	Co, 13.6; Ru, 1.1		

[1] Reverse micele impregnation
[2] Aqueous impregnation

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
63	1	18	15	0	0	2.5	7.0
69	1	10	13	0	0	3.0	5.0
	2	30	13	1.3	0.3	2.4	5.5
	3	50	11	1.5	0.8	1.2	6.2
72	1	8	19	3.0	0	4.5	9.0
	2	28	16	2.6	0.6	3.5	7.5
	3	99	9	1.7	0	3.1	1.0
68	1	20	21	5.2	0	8.5	2.5
	2	33	35	6.0	0	11.0	1.3
73	1	20	15	3.0	0	4.0	1.0
	2	22	75	13.0	0	22.0	2.0
	3	100	37	6.0	0	8.0	0
67	1	25	22	1.8	0	3.5	4.2
	2	50	20	1.9	0	4.0	3.7
	3	60	18	1.8	0	3.7	3.5
77	1	40	15	1.1	0	2.5	3.3
	2	75	20	1.9	0	3.6	4.0
	3	90	24	2.0	0	5.0	4.2

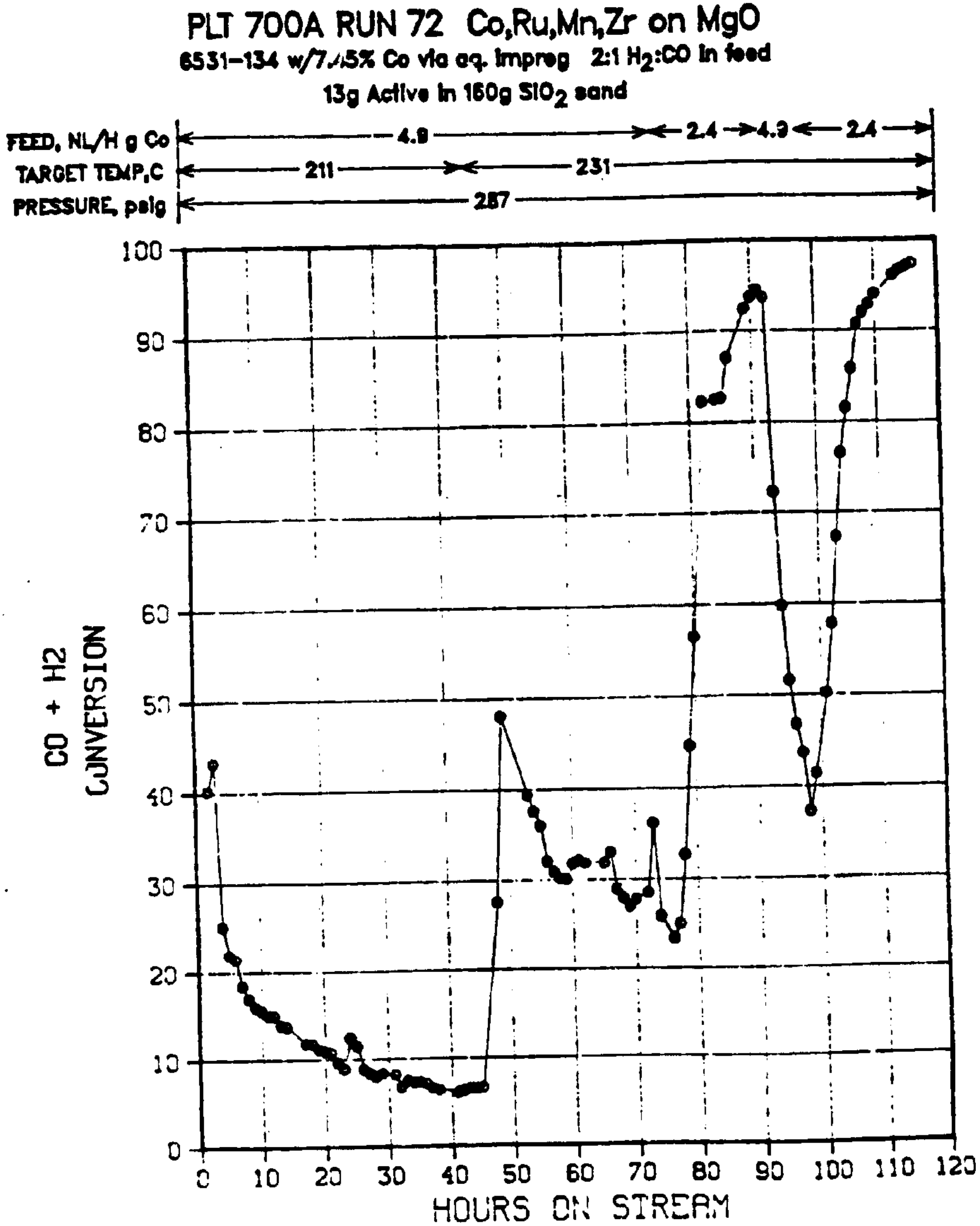
Table 4
Activity and Alcohol Selectivity of Catalysts

Run No.	Test Conditions	CO Conv., %	Alcohol Selectivity, %		
			C_1	C_3	C_4
65	1	58	0.5	0.2	0.2
63	1	18	1.6	0	1.0
69	1	10	2.5	0.5	1.6
	2	30	2.4	0.5	1.5
	3	50	1.5	0.5	1.5
72	1	8	0	0	0
	2	28	0	0	0
	3	99	2.0	0.7	1.5
68	1	20	3.8	1.0	1.8
	2	33	3.8	1.5	3.0
73	1	20	0.1	1.0	1.0
	2	22	6.0	4.0	6.0
	3	100	0	0	0
67	1	25	4.0	2.5	7.5
	2	50	2.0	1.1	2.5
	3	60	2.0	1.0	2.5
77	1	40	0.3	0.2	0.3
	2	75	0.3	0.2	0.4
	3	90	0.2	0.15	0.2

APPENDIX A

CATALYST PERFORMANCE DATA RUN SUMMARY

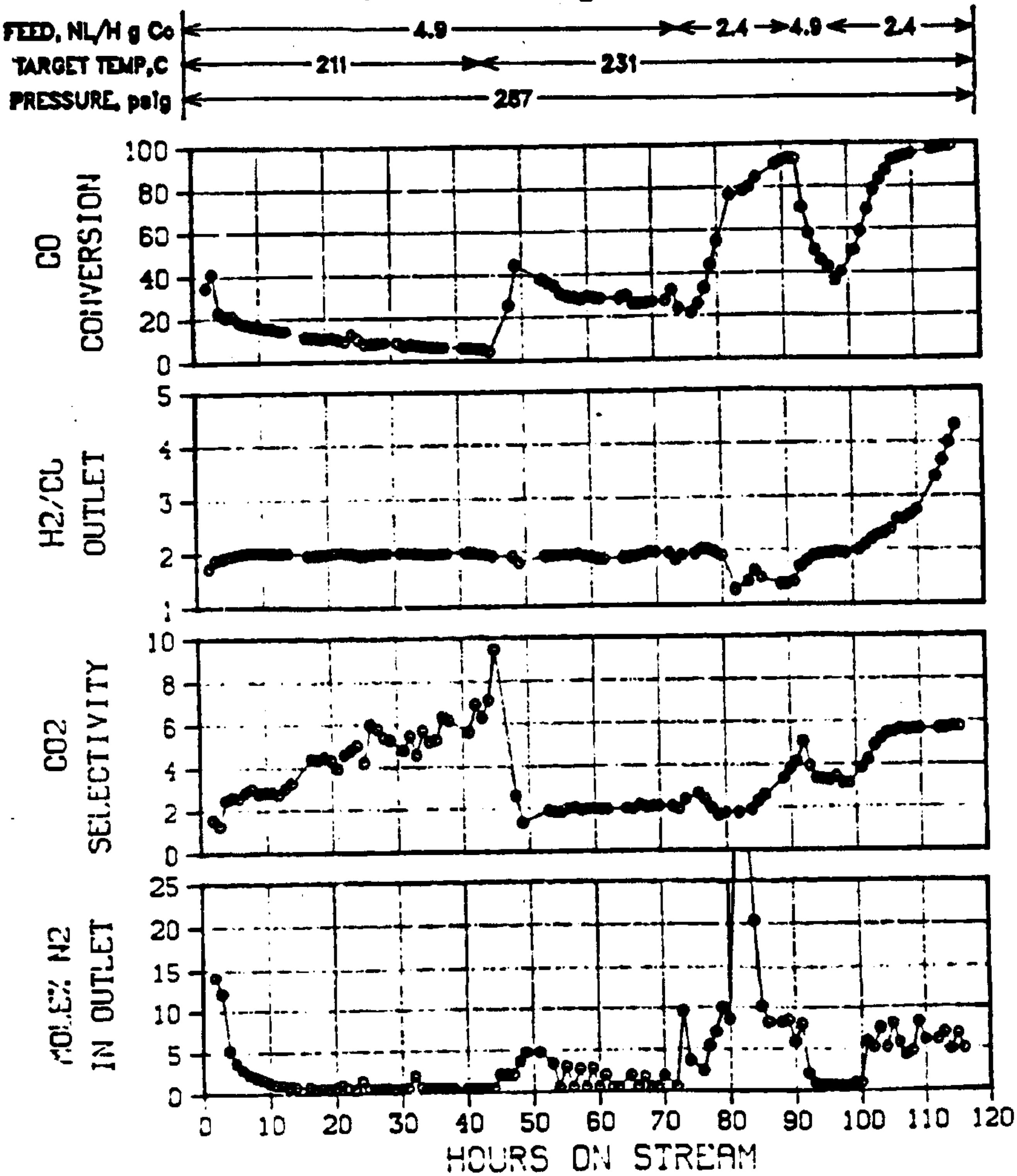
Figure 1


PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SIO2 sand
FEED, NL/H g Co
4.8
2.4
4.9
2.4
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO + H2
CONVERSION
HOURS ON STREAM
0
10
20
30
40
50
60
70
80
90
100
110
120

PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand



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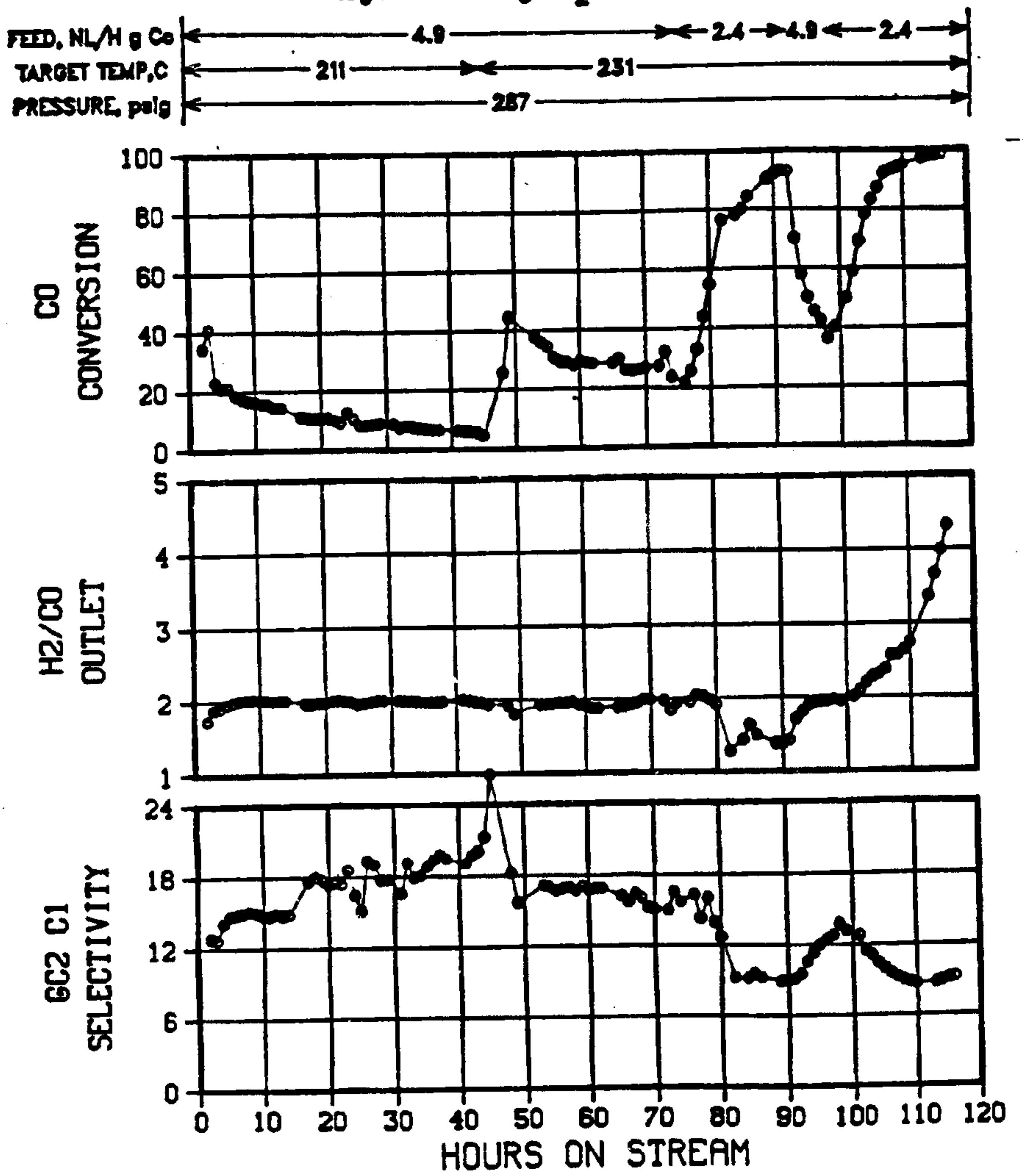
PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO

6531–134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

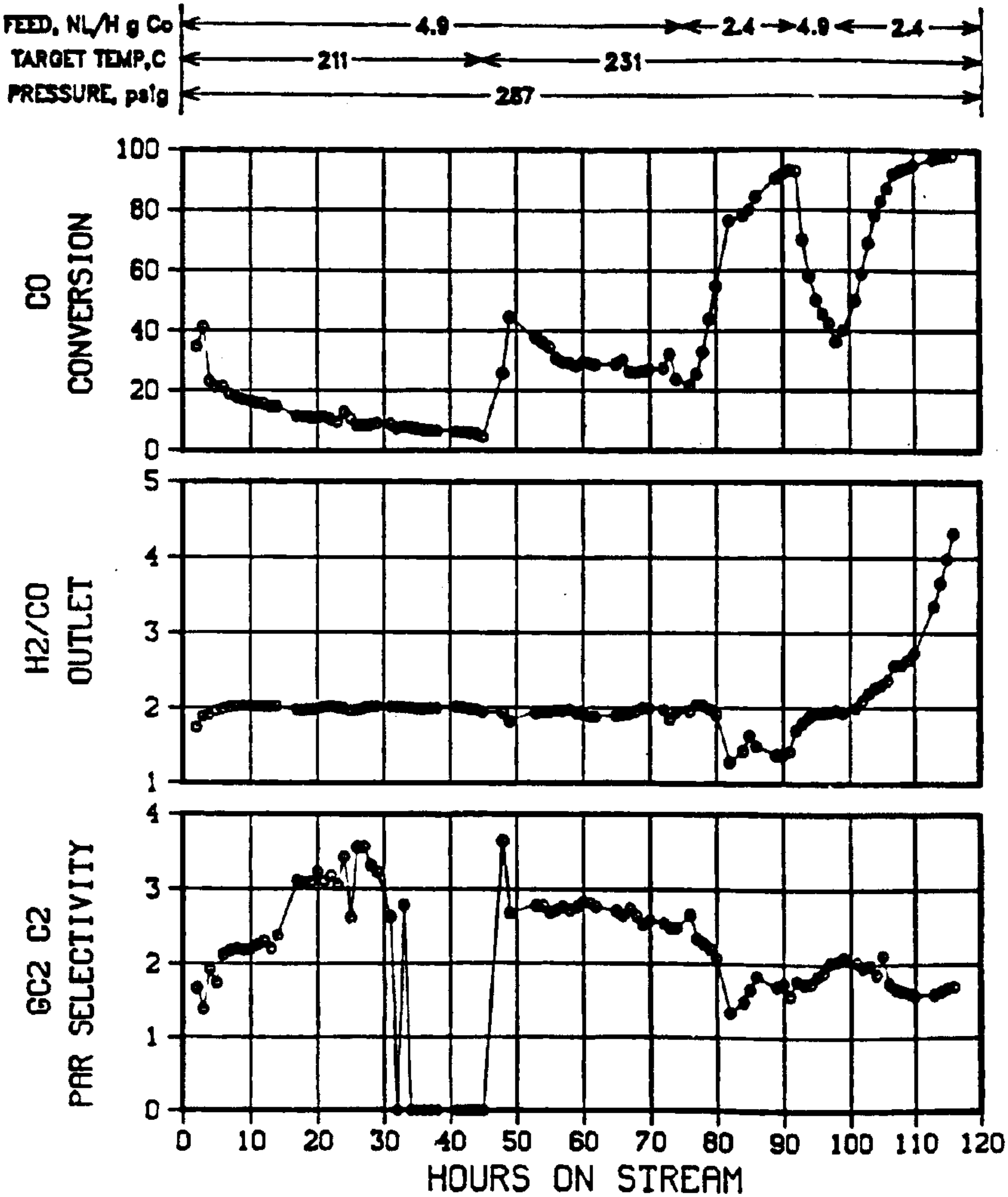
13g Active in 160g SiO_2 sand



PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand



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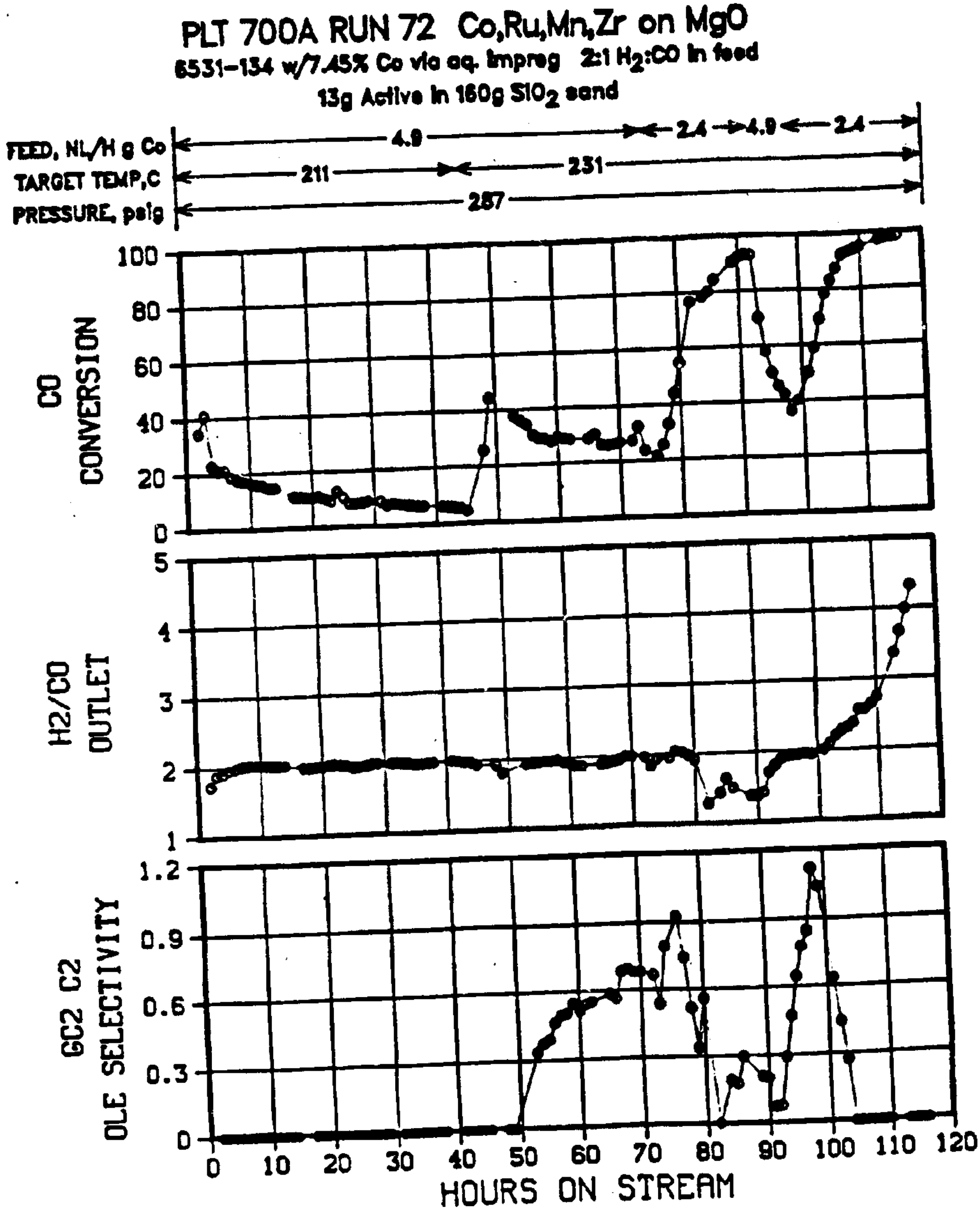
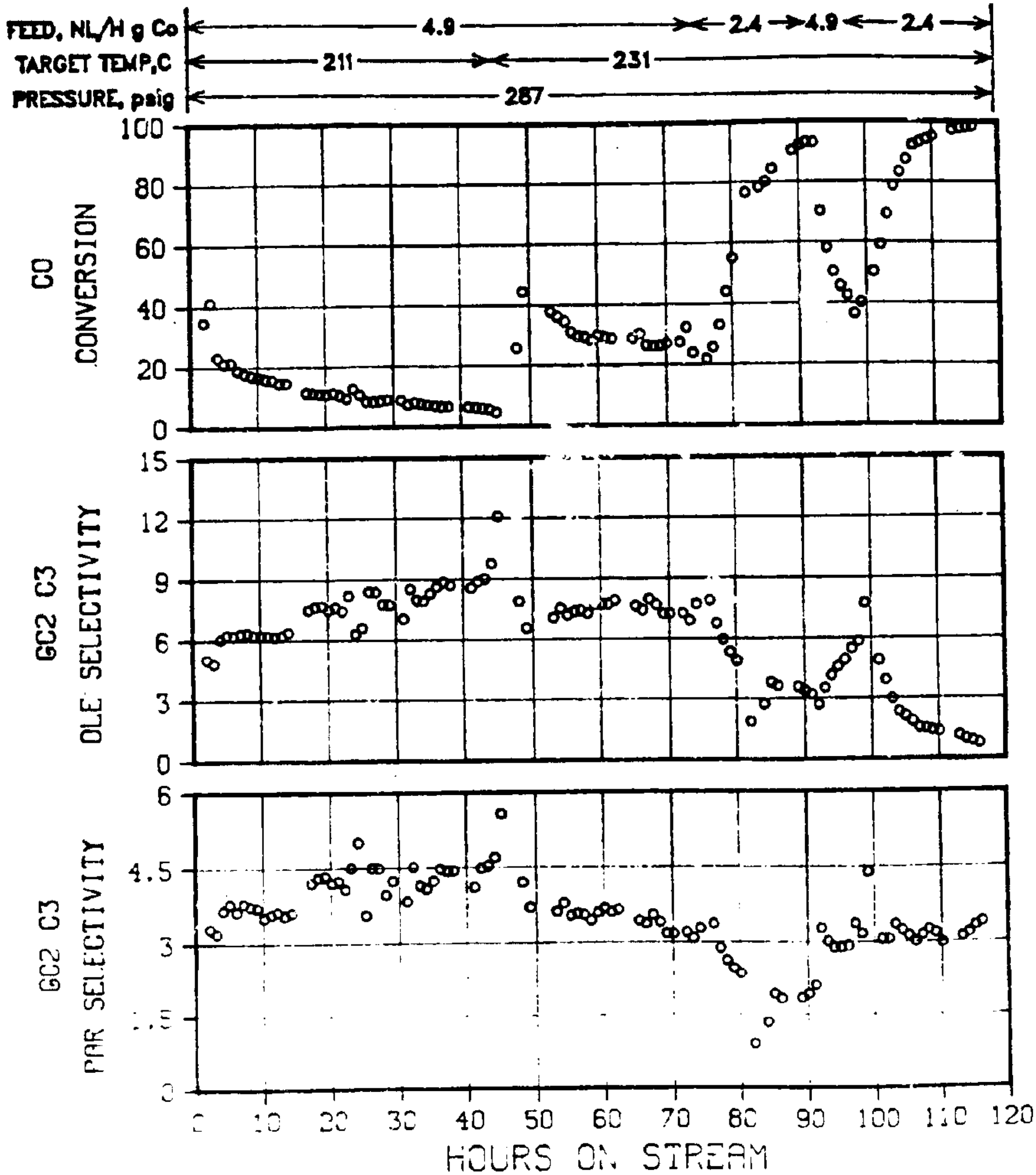

PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SiO2 sand
FEED, NL/H g Co
4.9
2.4
4.9
2.4
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
H2/CO OUTLET
GC2 C2 OLE SELECTIVITY
HOURS ON STREAM

PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO

6531–134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand



PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand

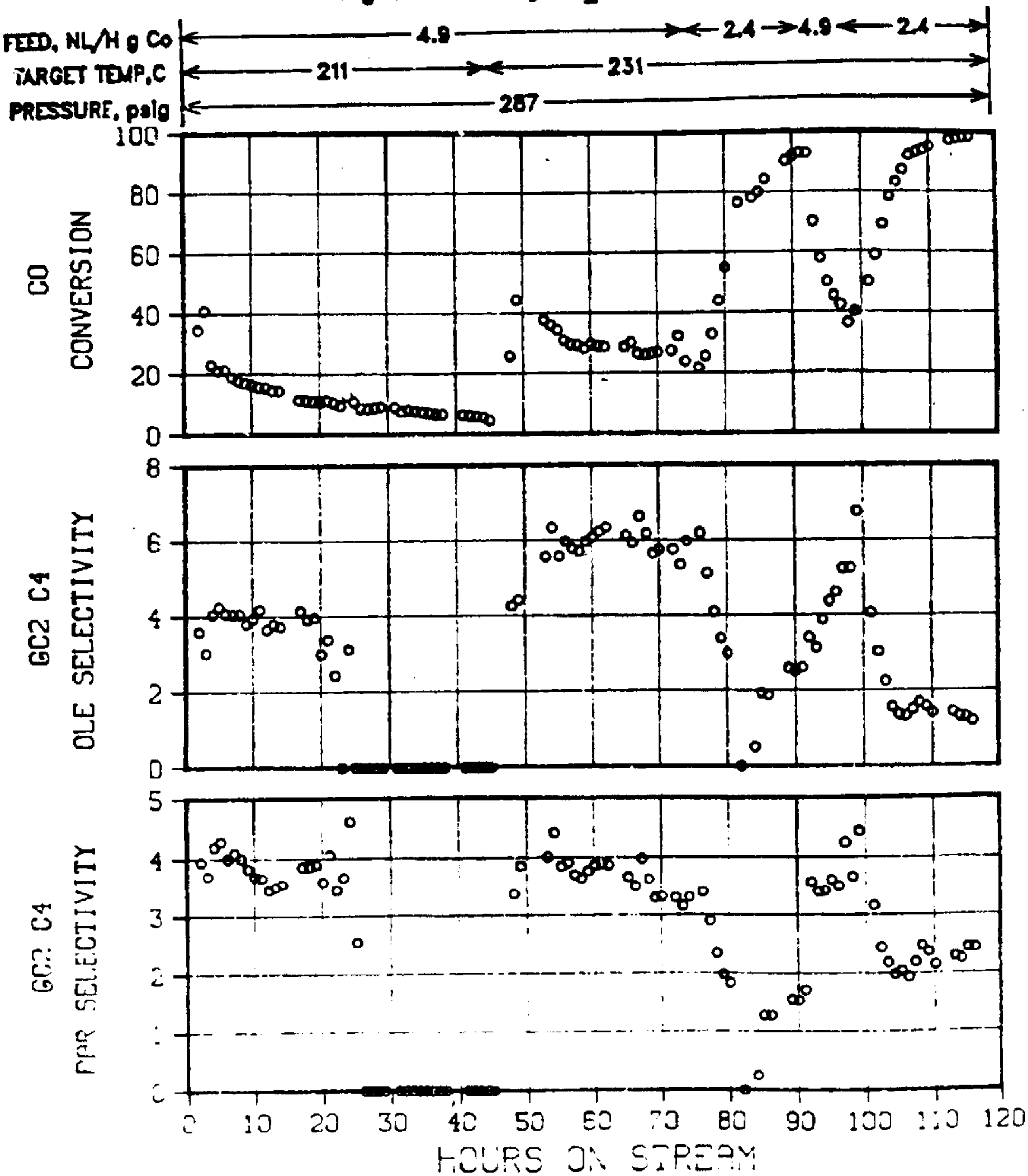
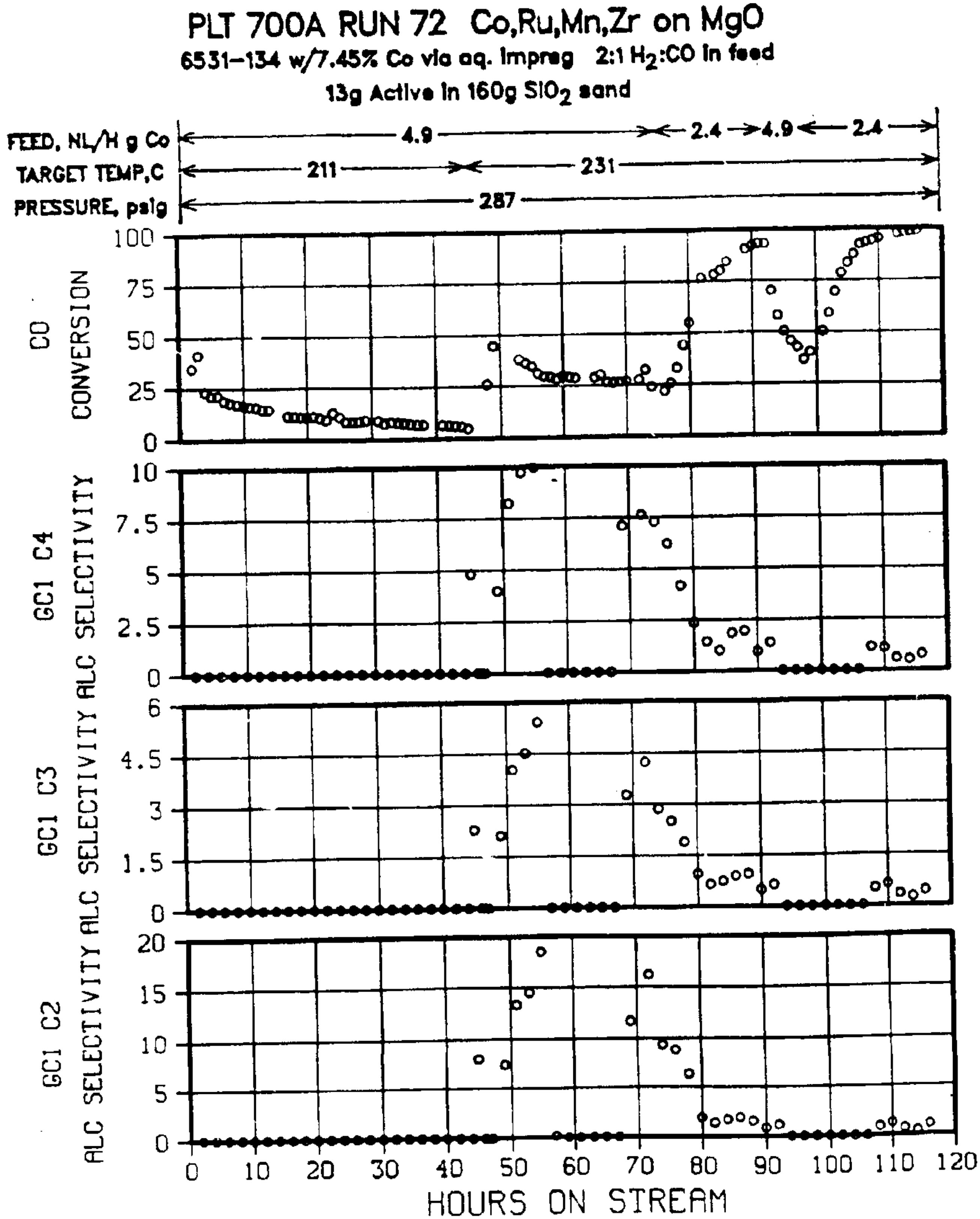


Figure 5



PLT 700A RUN 72 Co,Ru,Mn,Zr on MgO
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SiO2 sand
FEED, NL/H g Co
4.9
2.4
4.9
2.4
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
GC1 C4 ALC SELECTIVITY
GC1 C3 ALC SELECTIVITY
GC1 C2 ALC SELECTIVITY
HOURS ON STREAM

PLT 70JA RUN 73 Co,Ru on 50/50 Al_2O_3/TiO_2

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand

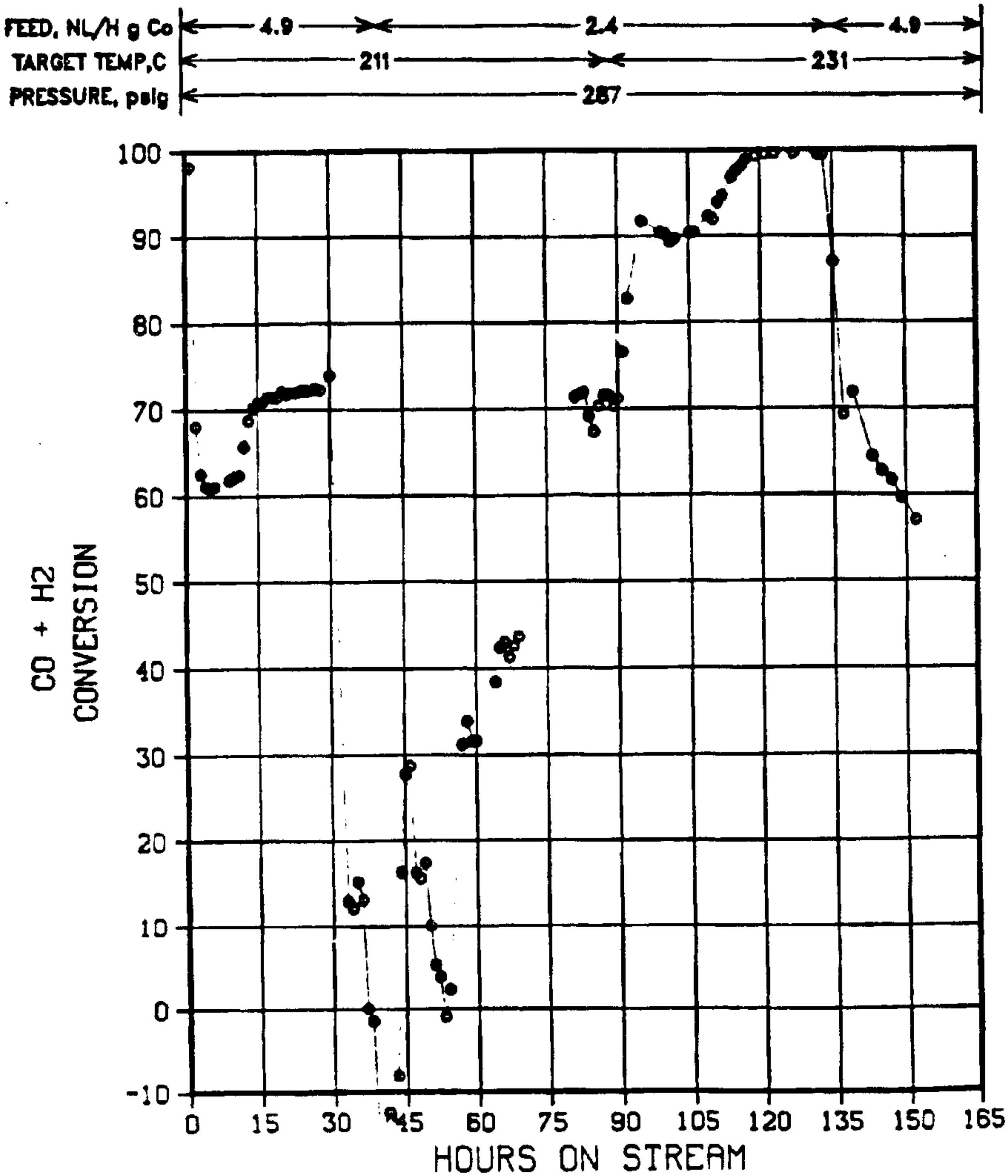


Figure 15

PLT 700A RUN 73 Co,Ru on 50/50 Al_2O_3/TiO_2

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand

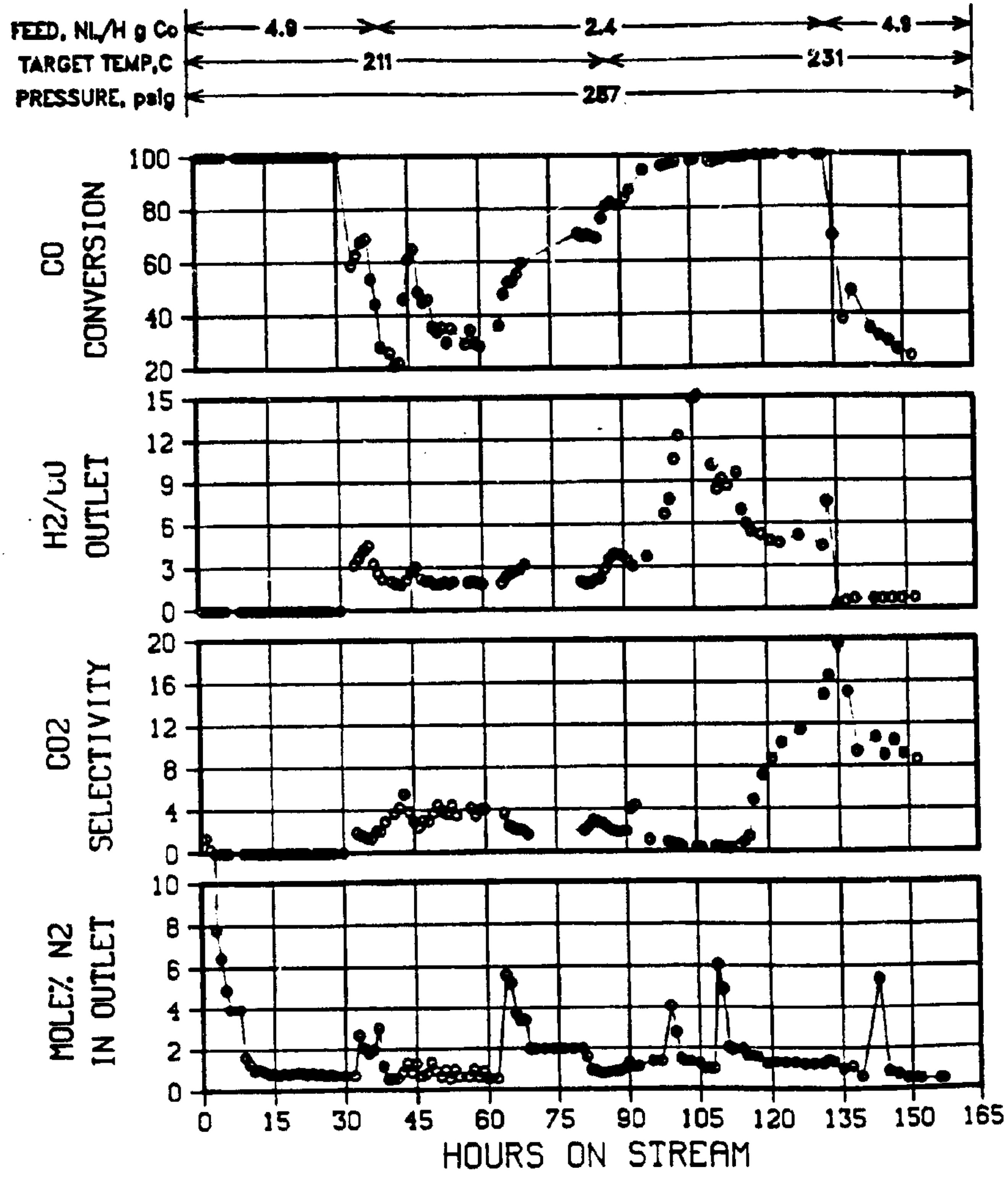
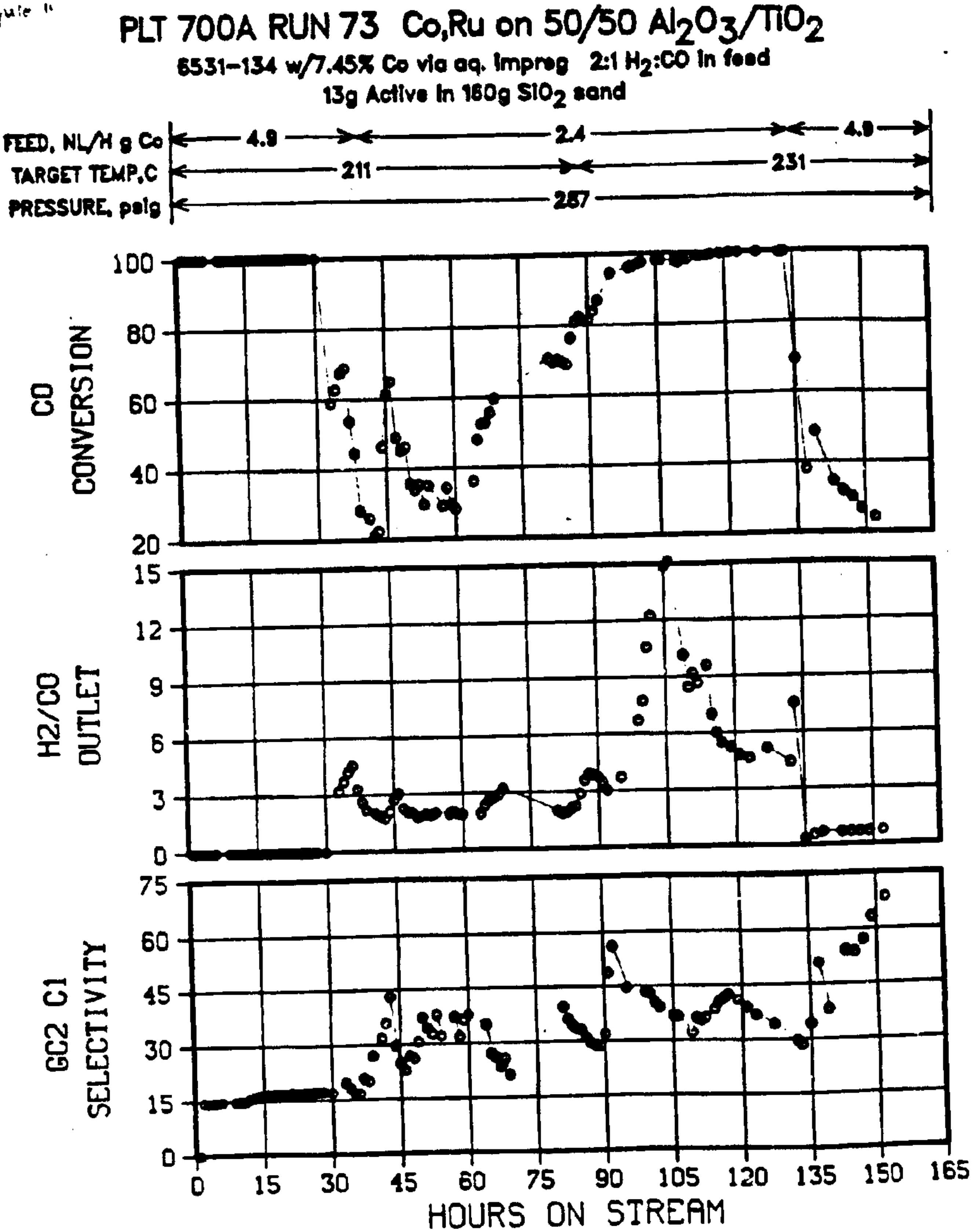
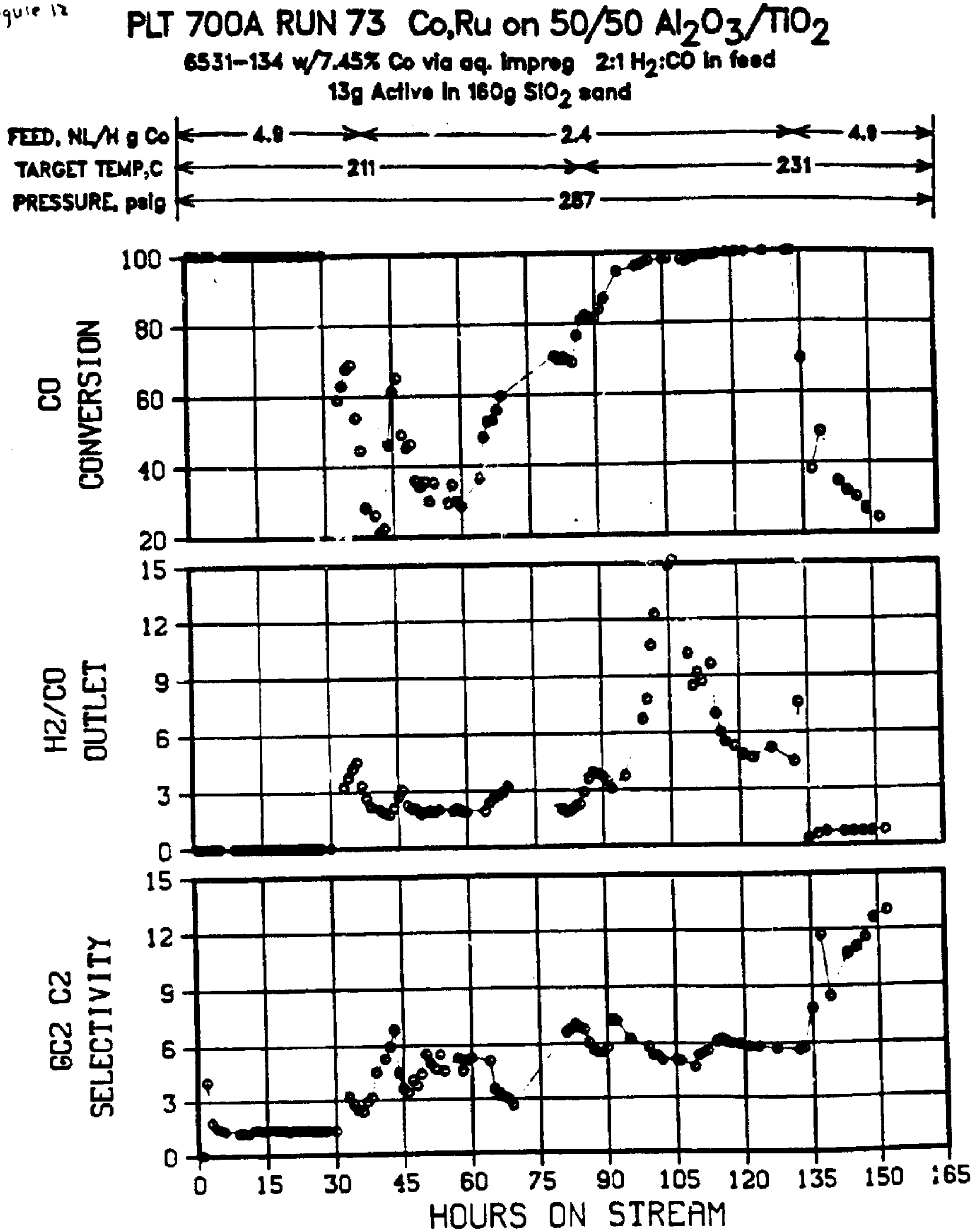


Figure 11



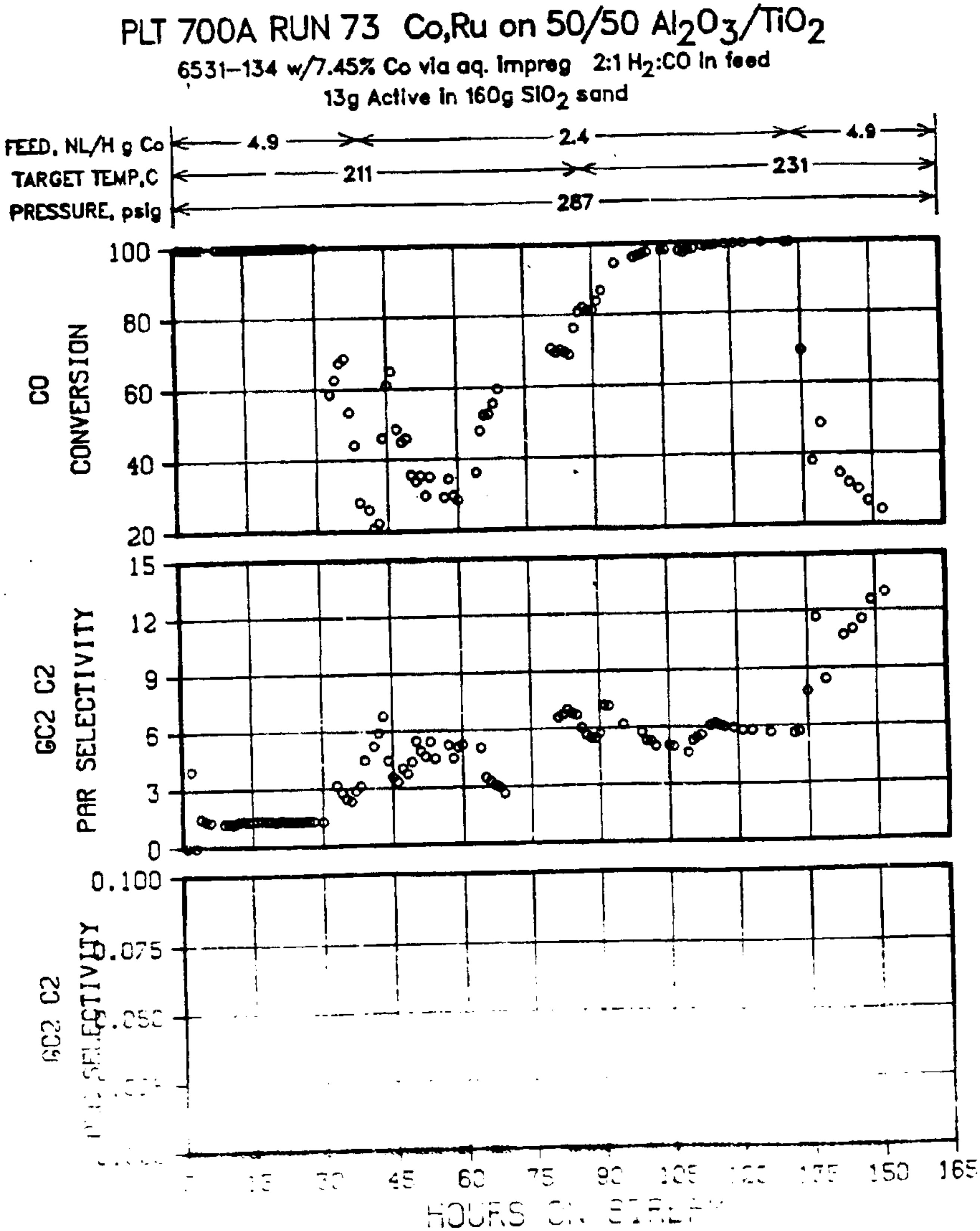
PLT 700A RUN 73 Co,Ru on 50/50 Al2O3/TiO2
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SiO2 sand
FEED, NL/H g Co
4.8
2.4
4.8
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
100
80
60
40
20
H2/CO OUTLET
15
12
9
6
3
0
GC2 C1 SELECTIVITY
75
60
45
30
15
0
0
15
30
45
60
75
90
105
120
135
150
165
HOURS ON STREAM

Figure 12



PLT 700A RUN 73 Co,Ru on 50/50 Al_2O_3/TiO_2
6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed
13g Active in 160g SiO_2 sand
FEED, NL/H g Co
4.8
2.4
4.8
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
H2/CO OUTLET
GC2 C2 SELECTIVITY
HOURS ON STREAM

Figure 13



PLT 700A RUN 73 Co,Ru on 50/50 Al2O3/TiO2
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SiO2 sand
FEED, NL/H g Co
4.9
2.4
4.9
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
100
80
60
40
20
GC2 C2 PAR SELECTIVITY
15
12
9
6
3
0
GC2 C2
0.100
0.075
15
45
60
75
150
165
HOURS

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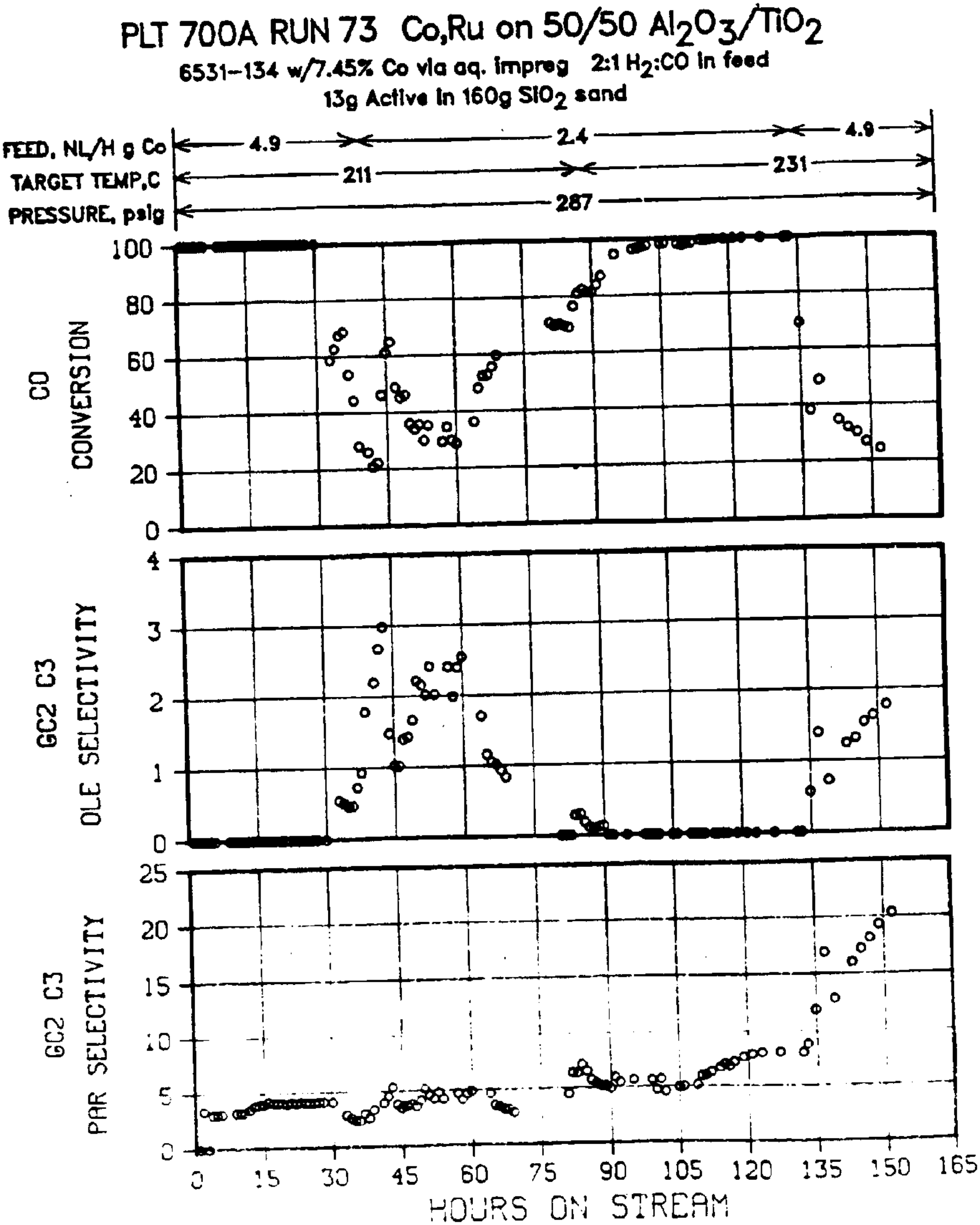
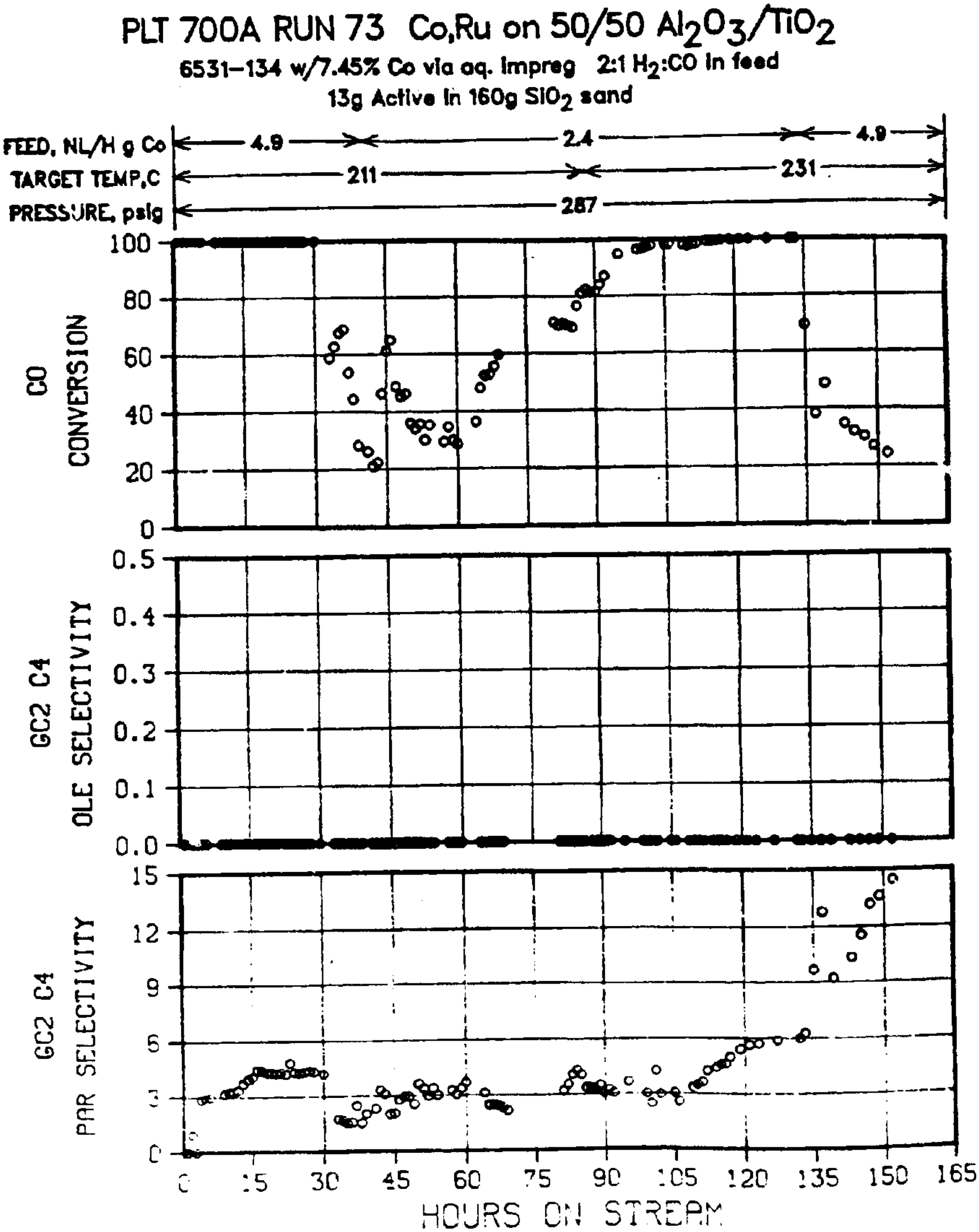

PLT 700A RUN 73 Co,Ru on 50/50 Al2O3/TiO2
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SiO2 sand
FEED, NL/H g Co
4.9
2.4
4.9
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
100
80
60
40
20
0
GC2 C3 OLE SELECTIVITY
4
3
2
1
0
GC2 C3 PAR SELECTIVITY
25
20
15
10
5
0
0 15 30 45 60 75 90 105 120 135 150 165
HOURS ON STREAM

Figure 15



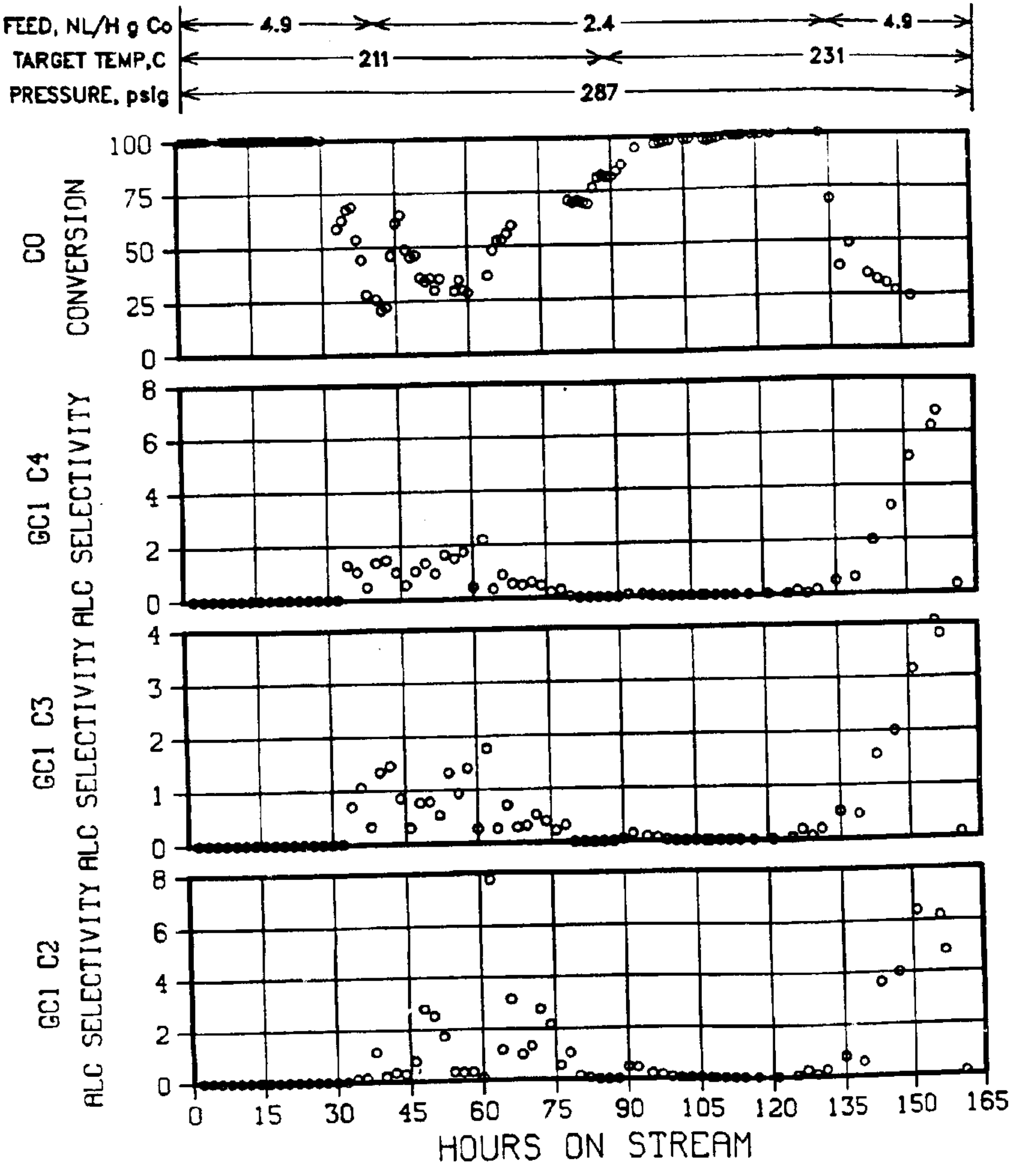
PLT 700A RUN 73 Co,Ru on 50/50 Al2O3/TiO2
6531-134 w/7.45% Co via aq. impreg 2:1 H2:CO in feed
13g Active in 160g SIO2 sand
FEED, NL/H g Co
4.9
2.4
4.9
TARGET TEMP,C
211
231
PRESSURE, psig
287
CO CONVERSION
100
80
60
40
20
0
GC2 C4 OLE SELECTIVITY
0.5
0.4
0.3
0.2
0.1
0.0
GC2 C4 PAR SELECTIVITY
15
12
9
6
3
0
0 15 30 45 60 75 90 105 120 135 150 165
HOURS ON STREAM

Figure 16

PLT 700A RUN 73 Co,Ru on 50/50 Al_2O_3/TiO_2

6531-134 w/7.45% Co via aq. impreg 2:1 H_2:CO in feed

13g Active in 160g SiO_2 sand



PLT 700A RUN 77 Co,Ru on Carbotrap B

6531–160 w/13.6 % Co via aq. impreg 2:1 H_2:CO in feed
13g active in 160g quartz sand

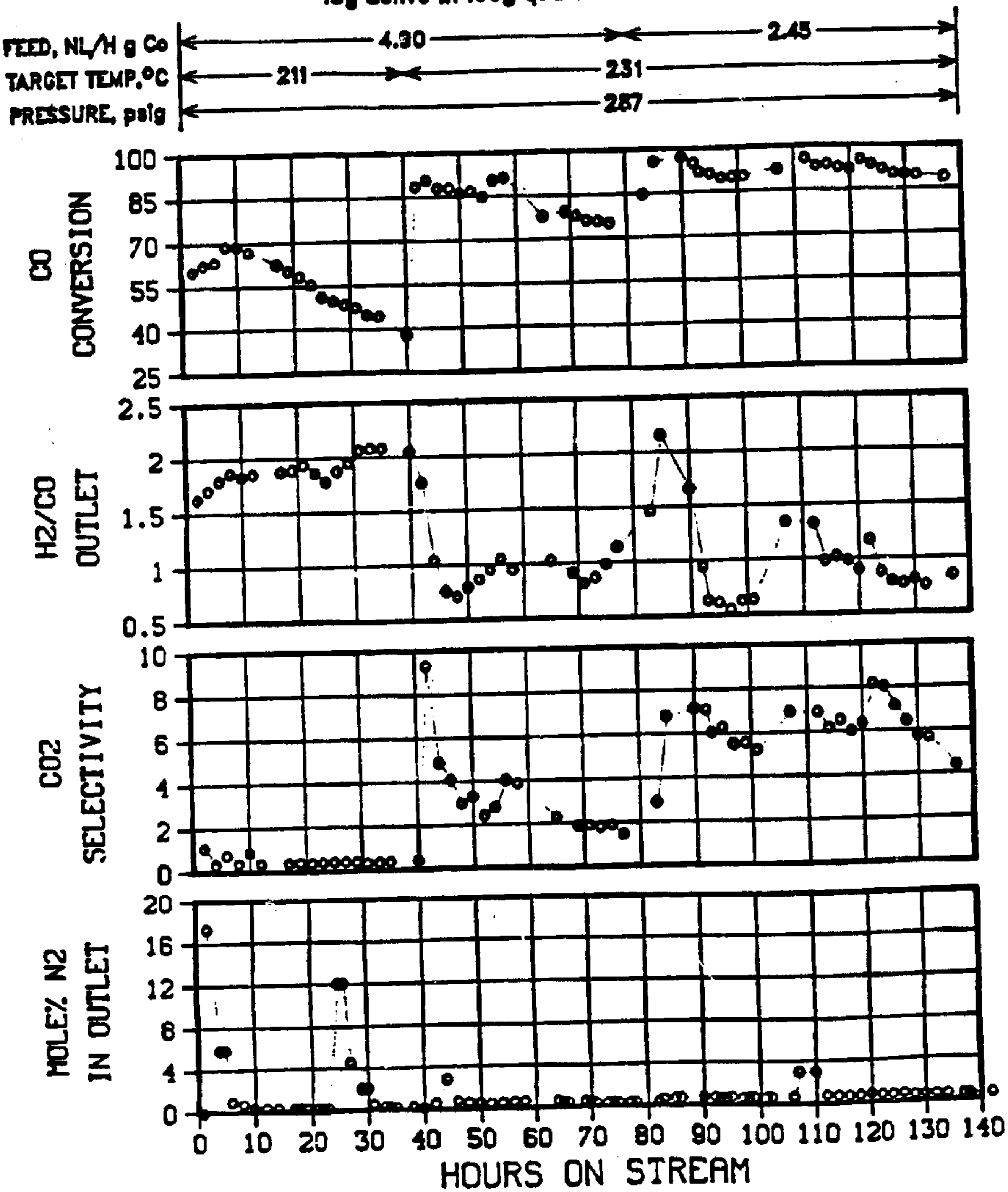
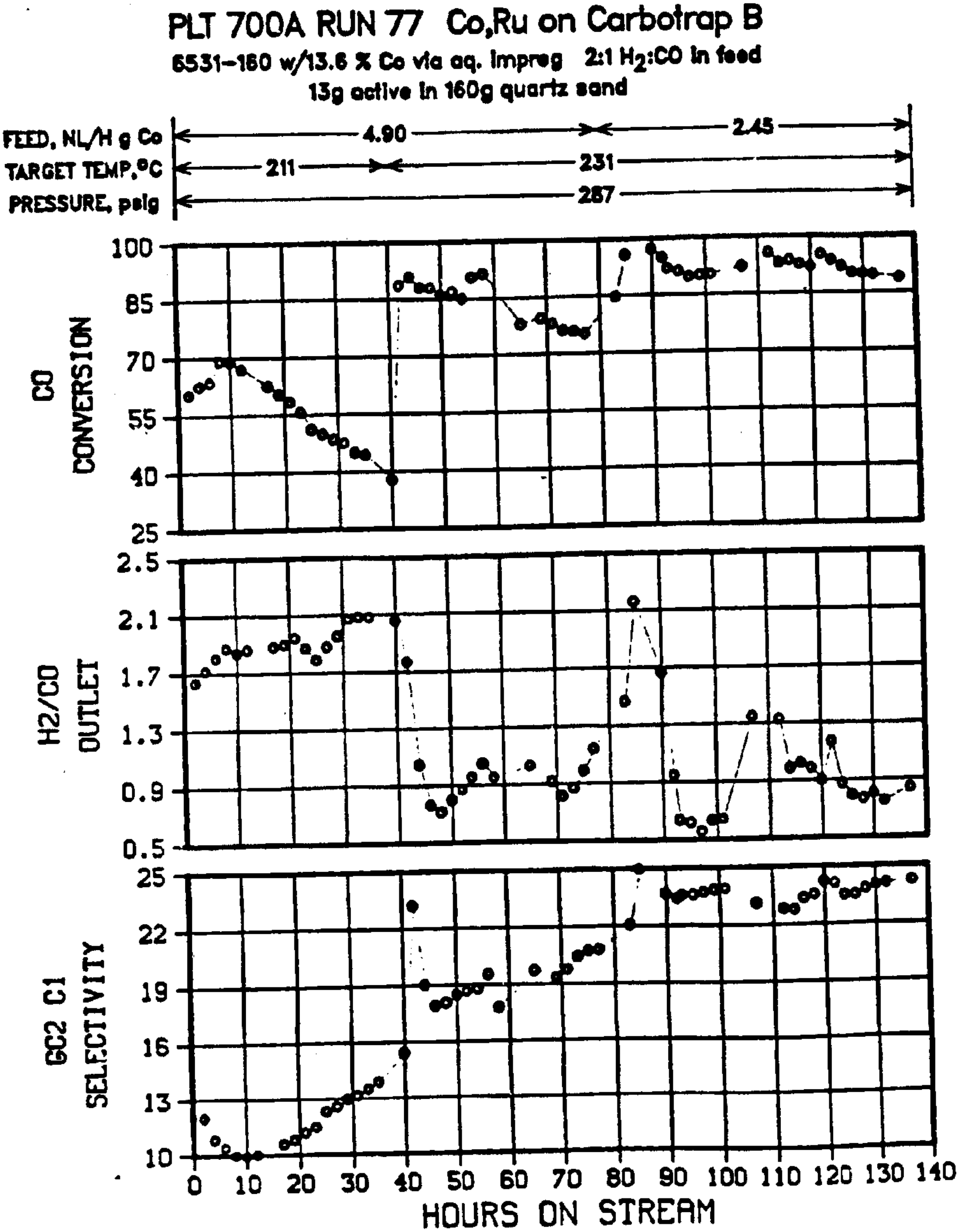


Figure 13

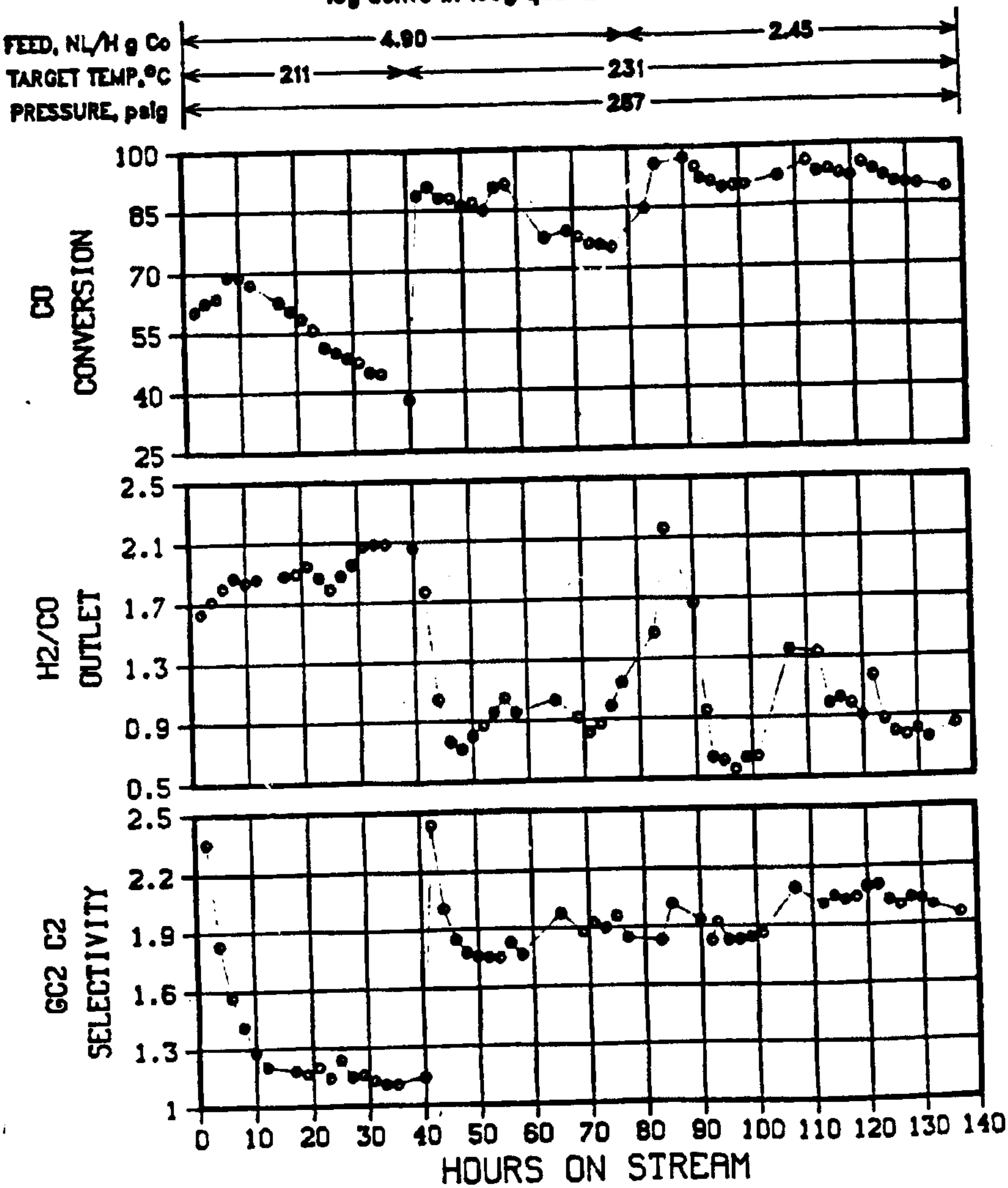


PLT 700A RUN 77 Co,Ru on Carbotrap B
6531-160 w/13.6 % Co via aq. impreg 2:1 H2:CO in feed
13g active in 160g quartz sand
FEED, NL/H g Co
4.90
2.45
TARGET TEMP,°C
211
231
PRESSURE, psig
287
CO CONVERSION
H2/CO OUTLET
GC2 C1 SELECTIVITY
HOURS ON STREAM

Figure 14

PLT 700A RUN 77 Co,Ru on Carbotrap B

6531-160 w/13.6 % Co via aq. impreg 2:1 H_2:CO in feed
13g active in 160g quartz sand



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PLT 700A RUN 77 Co,Ru on Carbotrap B

6531-160 w/13.6 % Co via aq. impreg 2:1 H_2:CO in feed
13g active in 160g quartz sand

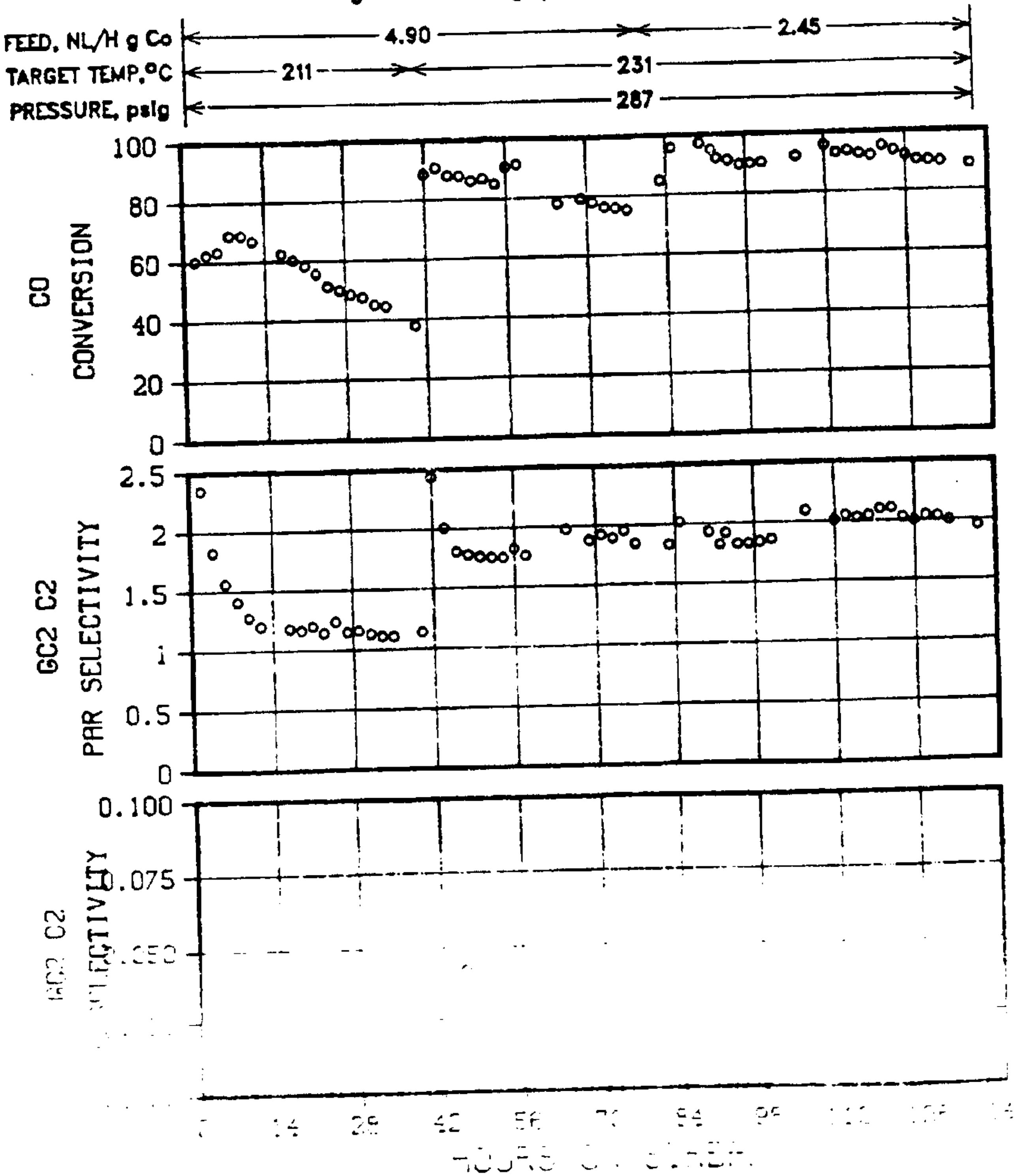


Figure 21

PLT 700A RUN 77 Co,Ru on Carbotrap B

6531-160 w/13.6 % Co via aq. impreg 2:1 H_2:CO in feed

13g active in 160g quartz sand

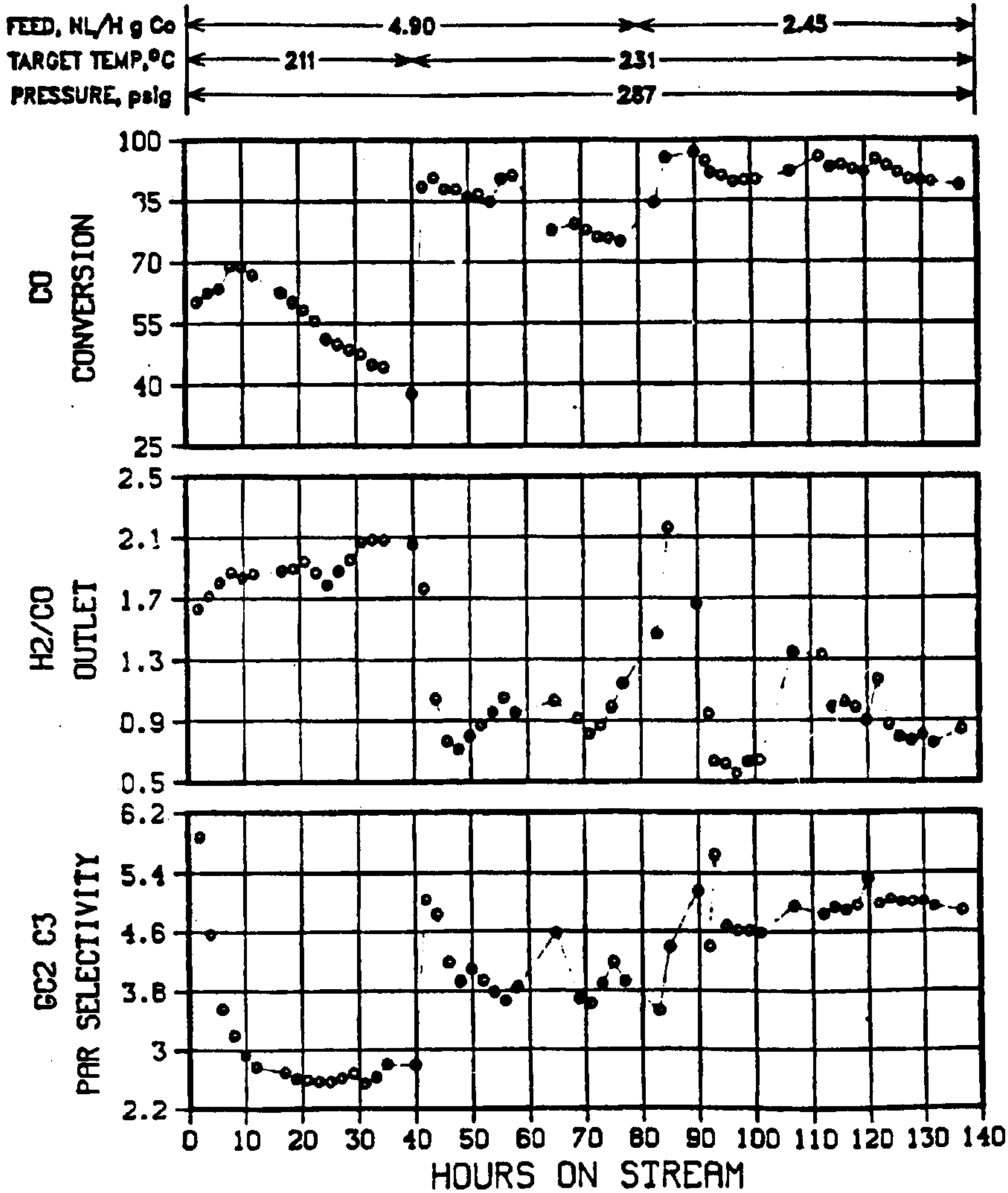


Figure 22

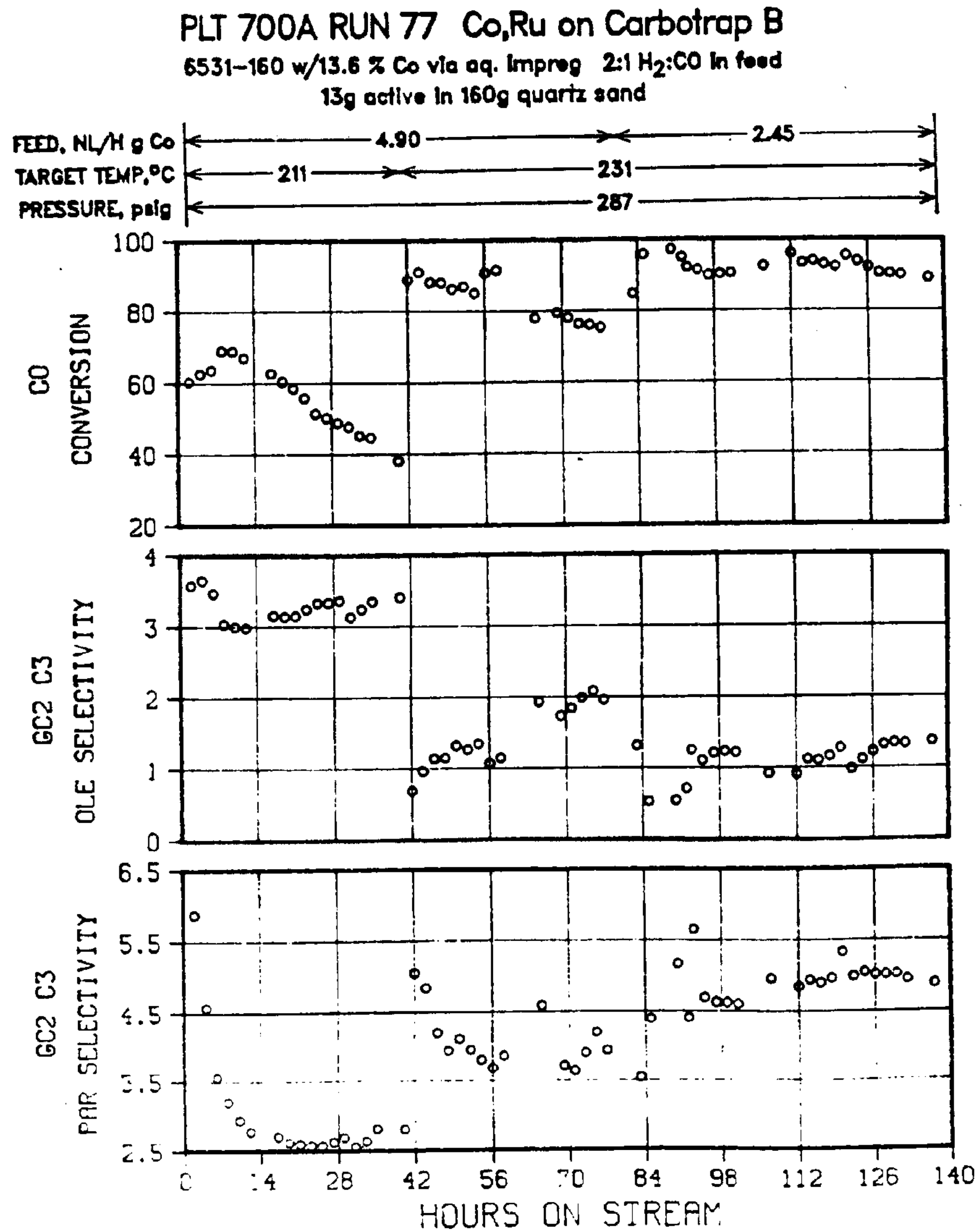
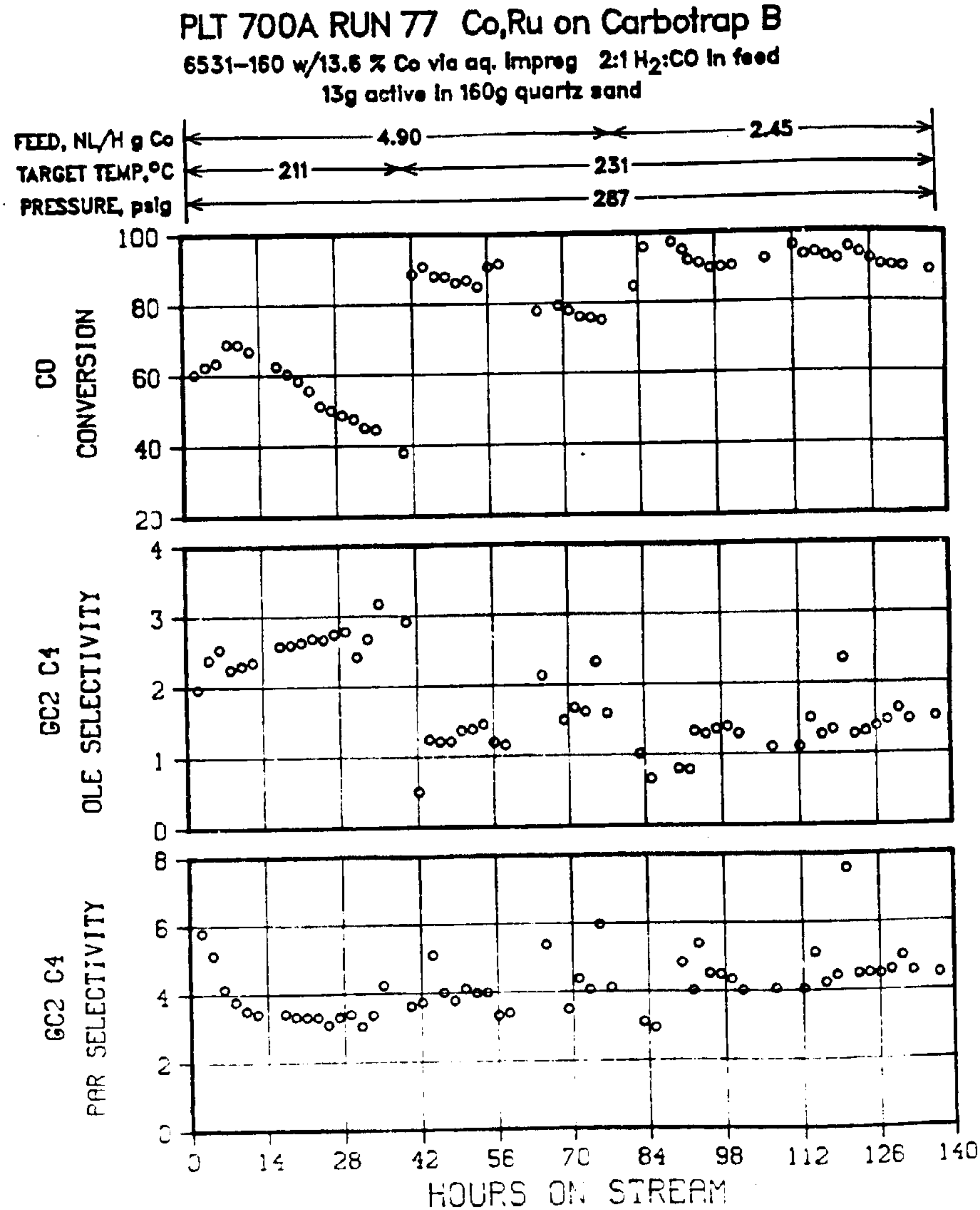

PLT 700A RUN 77 Co,Ru on Carbotrap B
6531-160 w/13.6 % Co via aq. impreg 2:1 H2:CO in feed
13g active in 160g quartz sand
FEED, NL/H g Co
4.90
2.45
TARGET TEMP, °C
211
231
PRESSURE, psig
287
CO CONVERSION
OLE SELECTIVITY GC2 C3
PAR SELECTIVITY GC2 C3
HOURS ON STREAM
0
14
28
42
56
70
84
98
112
126
140
100
80
60
40
20
4
3
2
1
0
6.5
5.5
4.5
3.5
2.5

Figure 23



PLT 700A RUN 77 Co,Ru on Carbotrap B
6531-160 w/13.6 % Co via aq. impreg 2:1 H2:CO in feed
13g active in 160g quartz sand
FEED, NL/H g Co
4.90
2.45
TARGET TEMP,°C
211
231
PRESSURE, psig
287
CO CONVERSION
GC2 C4 OLE SELECTIVITY
GC2 C4 PAR SELECTIVITY
HOURS ON STREAM

PLT 700A RUN 77 Co,Ru on Carbotrap B

6531-160 w/13.6 % Co via aq. impreg 2:1 H_2:CO in feed
13g active in 160g quartz sand