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DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

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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.

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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

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Experimental

In this report three runs are described, all were performed in the fixed-bed pilot plant. 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 GC which analyzed the gas product.

The feed for all cobalt catalyst evaluations was a blend of hydrogen, carbon monoxide and argon. The argon was an internal standard used for calculating conversions and selectivities. The molar ratio of hydrogen to carbon monoxide was two, which is typical of a methane-derived synthesis gas. A typical feed was comprised of the following mole percentages of gases: hydrogen 64, carbon monoxide 31, argon 5. Because of the sensitivity of Fischer-Tropsch catalysts to feed impurities, pure feeds were purchased from Scott Specialty Gases of Troy MI. Furthermore, prior to use the feed was processed through 1265 cc of alumina spheres at 210° C and 515 cc of 13X zeolites at room temperature.

The catalyst was prepared via the steps of: impregnation, calcination, and reduction. The support was a special Y zeolite-derived material. The impregnation step consisted of pore filling with an ethylene glycol solution of metal salts followed by evaporation of the solvent. The calcination after impregnation was four hours at 450° C. The reduction step (activation) was the final one before introduction of the Fischer-Tropsch feed. This step was accomplished after the catalyst and a diluent (quartz sand) were loaded; it consisted of four hours of flowing hydrogen. Each of the three catalysts resulted from a different temperature during this reduction step. The diluent aids removal of heat resulting from the very

exothermic nature of the Fischer-Tropsch reactions.

Powdery catalyst (13 g) was loaded with 160 g of the 60 to 80 mesh quartz sand diluent. A thermowell was present down the center of the catalyst/diluent bed. A sliding thermocouple in this well allowed bed temperature profiles to be obtained. Previous experimental catalysts were screened in the fixed-bed pilot plant via a three condition test. The final two (more strenuous) conditions were needed to achieve high conversions since the catalysts were of low activity. High conversions are required because high conversion hydrocarbon selectivities (particularly methane) are needed to properly evaluate a catalyst. The catalysts described in this report were very active and needed, therefore, only to be screened at the initial condition.

All figures including run summary plots of conversions and selectivities vs. hours-on-stream are attached in Appendix A.

Scope of Work During Reporting Period

The catalysts discussed in this report were prepared on a steamed Y zeolite that had been washed three hours with 4M hydrochloric acid. This resulted in minimal loss in zeolite crystallinity. The purpose of acid-washing is to remove pore-obstructing alumina debris which results from steaming. Acid washing must be properly managed; if it is too strenuous the crystallinity remaining after steaming is destroyed and an amorphous silica results. Hydrochloric acid is particularly prone to destroying zeolite crystallinity. However, if the wash is of short duration little crystallinity is lost. A successful wash is one that removes aluminum but does not produce significant changes in surface area, pore volume or % crystallinity by X-Ray analysis.

The catalysts contained ruthenium in addition to cobalt since it is an objective of this work to determine whether incorporation of a small amount of ruthenium can result in high activity catalysts.

Steamed Y zeolite contains steaming-derived amorphous pores that are from 50 to 100 Å in diameter in addition to the remaining crystalline channels and cages of the original Y zeolite. The amorphous pores are large enough to support 50-100 Å cobalt crystallites, a size considered optimal for Fischer-Tropsch catalysis.

Previous quarterly reports described very high activity Fischer-Tropsch (F-T) catalysts which resulted from impregnation of about 18 wt% cobalt and a lower level of ruthenium onto a steamed/acid-washed Y zeolite support. It was the objective of this quarter's work to determine whether changing the catalyst activation conditions could enhance the activity or selectivity of the catalysts.

The activation procedure used for all previous catalysts in this contract is outlined in Figure A-1. The final step, namely the two hour reduction at 350° C, is the one which was varied in this study. Catalysts were prepared by two hour reductions at, respectively, 325° C and 375° C.

Properties of the supports and metals-impregnated materials before reduction are tabulated in Figure A-2.

Results and Discussion

Run 97

This run used a catalyst that was reduced at 350° C. By the end of this 130 hour run the rate of activity loss was low (Figure A-3), in addition, the selectivities had also stabilized (Figures A-4 to A-7). The very active nature of the catalyst is witnessed by the catalyst bed temperature profiles in Figure A-8.

Even with the silica diluent the catalyst bed maximum temperature was significantly above the inlet temperature showing that even better heat dissipation is required.

Run 104

The catalyst used in this run was reduced at 325° C. It was a short run like Run 97, but as in this previous run the activity (Figures A-9 and A-10) and selectivities (Figures A-11 to A-14) had stabilized by run's end. This catalyst was not quite as active as the one above. It is possible that there were slight differences in the two supports since they resulted from different washings of the same steamed Y zeolite. However, it is more likely that the lower reduction temperature was not as effective. Additional low temperature reductions should be performed but for longer periods of time. The selectivities at the end of Runs 97 and 104 were similar, and are compared in tabular fashion in Figure A-15.

Run 102

This run used a catalyst that had been reduced at 375° C. It was also evaluated in a short run. In this case the rate of deactivation was still fairly rapid at run's end (Figures A-16 and A-17). This resulted in final conversions that were quite low compared to those in Runs 97 and 104. With the possible exception of ethylene, the selectivities had stabilized by the end of the run (Figures A-18 to A-21). End of run performance results for this run are also tabulated in Figure A-15. It appears that high temperature catalyst reductions with hydrogen should be avoided.

Summary and Implications for Further Work

Initial experiments have been performed to determine the best activation procedure for the high cobalt, high activity, Y zeolite-supported F-T catalyst. At this time the temperature used for the lower cobalt-level catalyst appears to be the best. Future activation experiments should be done at lower temperatures,

· but for longer periods of time.

The runs outlined in this report and several in earlier reports were done with the standard reactor loading of 13 g but with high activity catalysts. In all of these runs a significant temperature exotherm was observed on the catalyst bed. In future runs less catalyst will be used with the same or more quartz sand diluent. This should reduce or eliminate the catalyst bed exotherm and make it easier to evaluate two different catalysts at the same temperature.

APPENDIX A

FIGURE A-1
STANDARD CATALYST PREPARATION

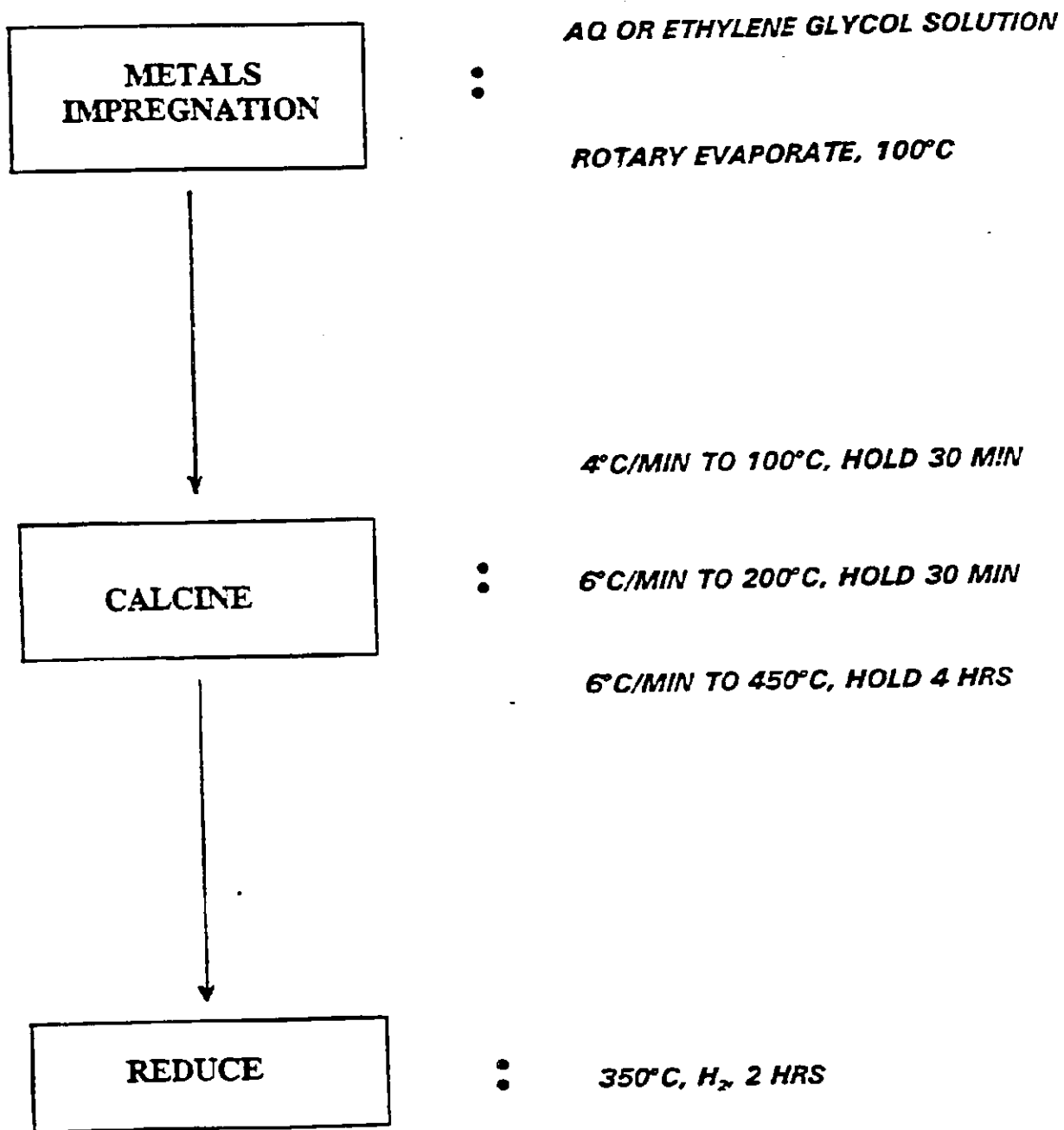


FIGURE A-2

CATALYST PRECURSORS:
SUPPORTED OXIDES ON STEAMED/ACID-WASHED Y ZEOLITES

SUPPORT PROPERTIES				CATALYST NO./ RUN NO.	CATALYST METALS, AAS WT%			
TRTMNTS	X-RAY ¹	SA ² /PV ³	Al ⁴		Co	Mn	Zr	Ru
STMD/ HCl ⁷	84.2 ± 0.3	582/0.56	0.46	6827-81/97	17.6	2.0	1.6	1.0
	84.5 ± 0.3	574/0.54	0.48	6827-99/102, 104	18.5	2.2	2.0	1.3

1. ABSOLUTE INTENSITY VS. LZ 210 (UNSTEAMED Y ZEOLITE) WHICH = 99.7 ± 1.7.

2. m²/g

3. cc/g

4. wt %

5. WASH 72 HOURS WITH 3M HNO₃.

6. THIS CATALYST ALSO CONTAINED 0.43 wt% RHENIUM.

7. WASH 3 HOURS WITH 4M HCl.

FIGURE A-3
PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

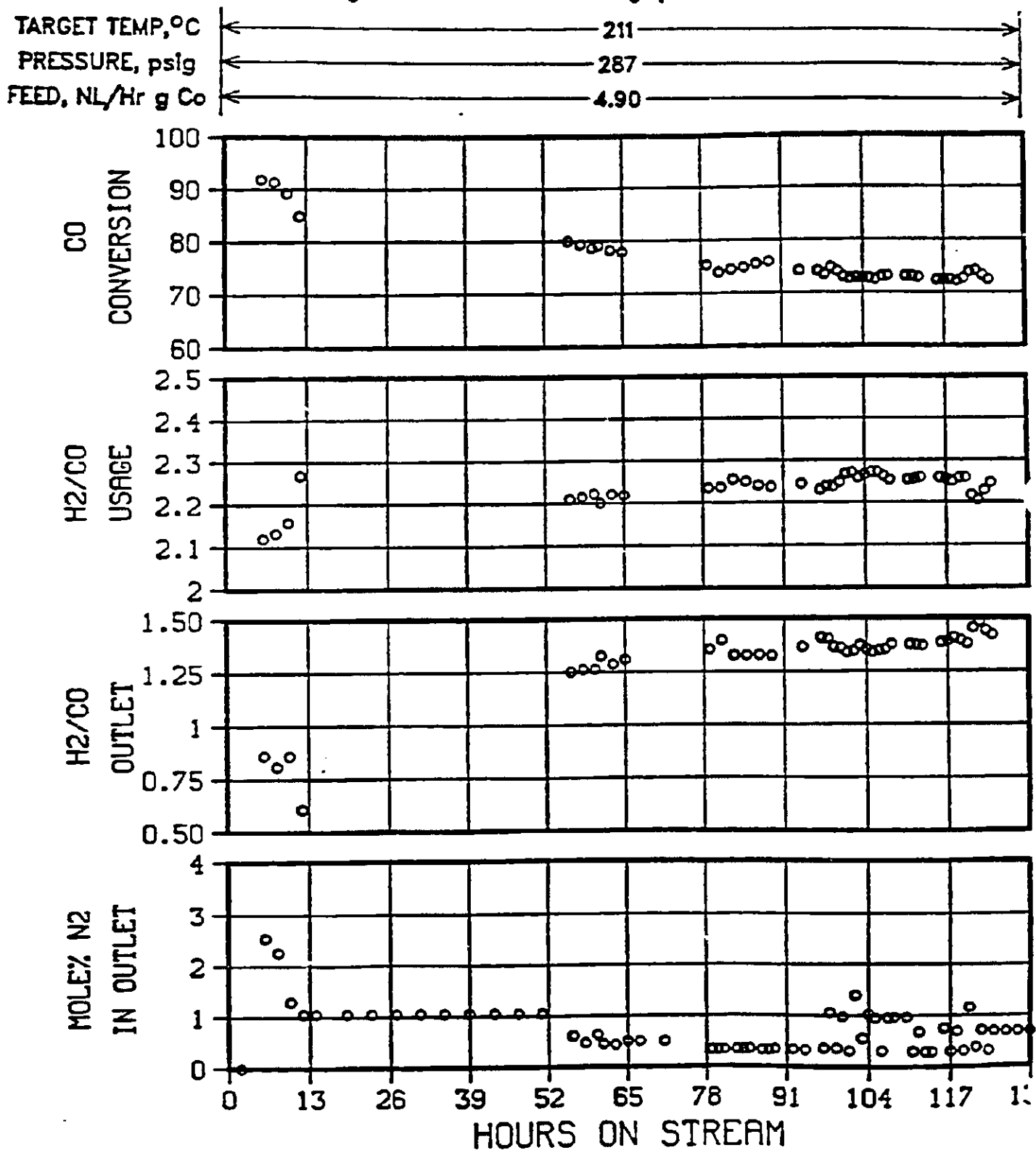


FIGURE A-4
PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

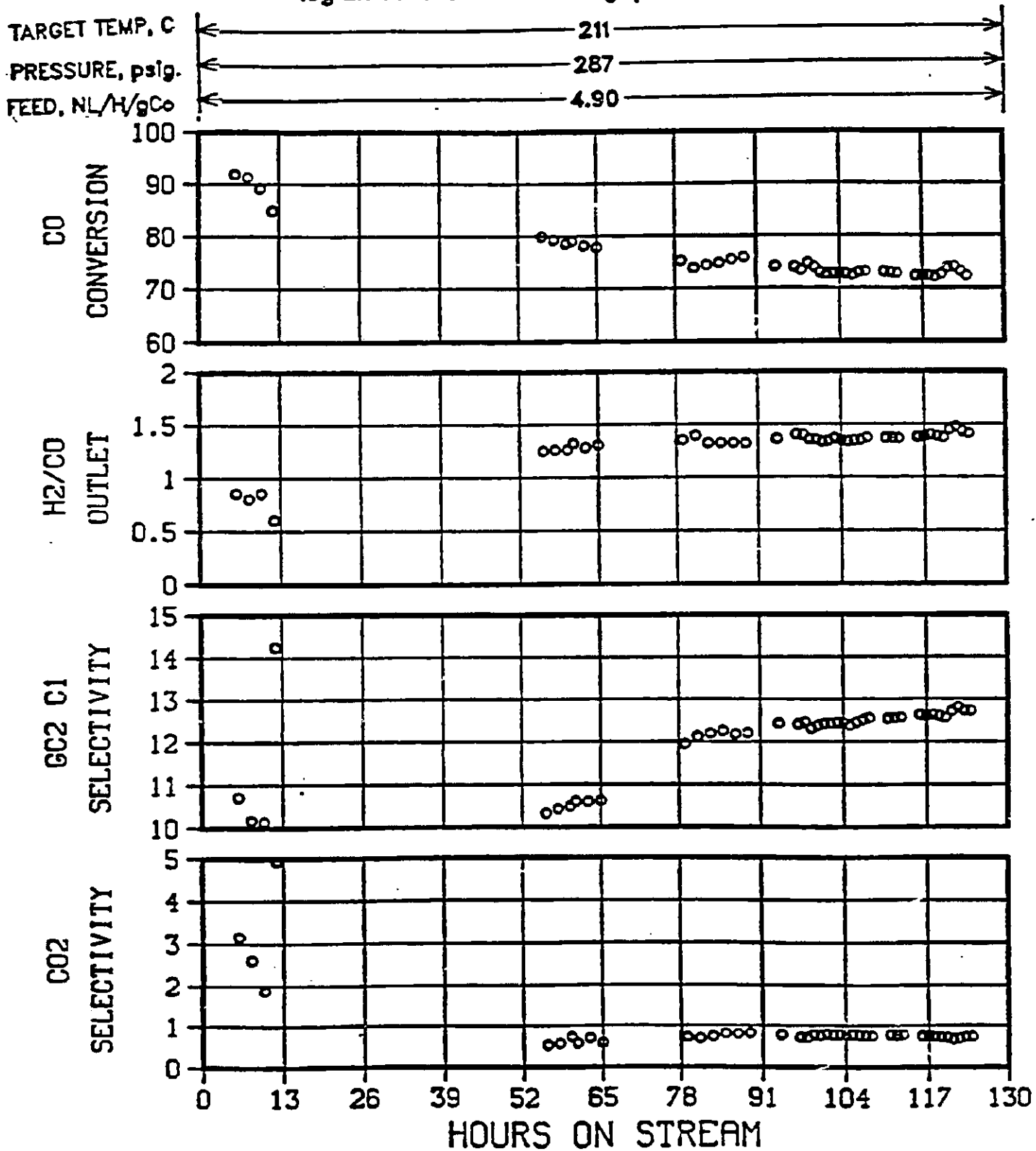


FIGURE A-5
PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

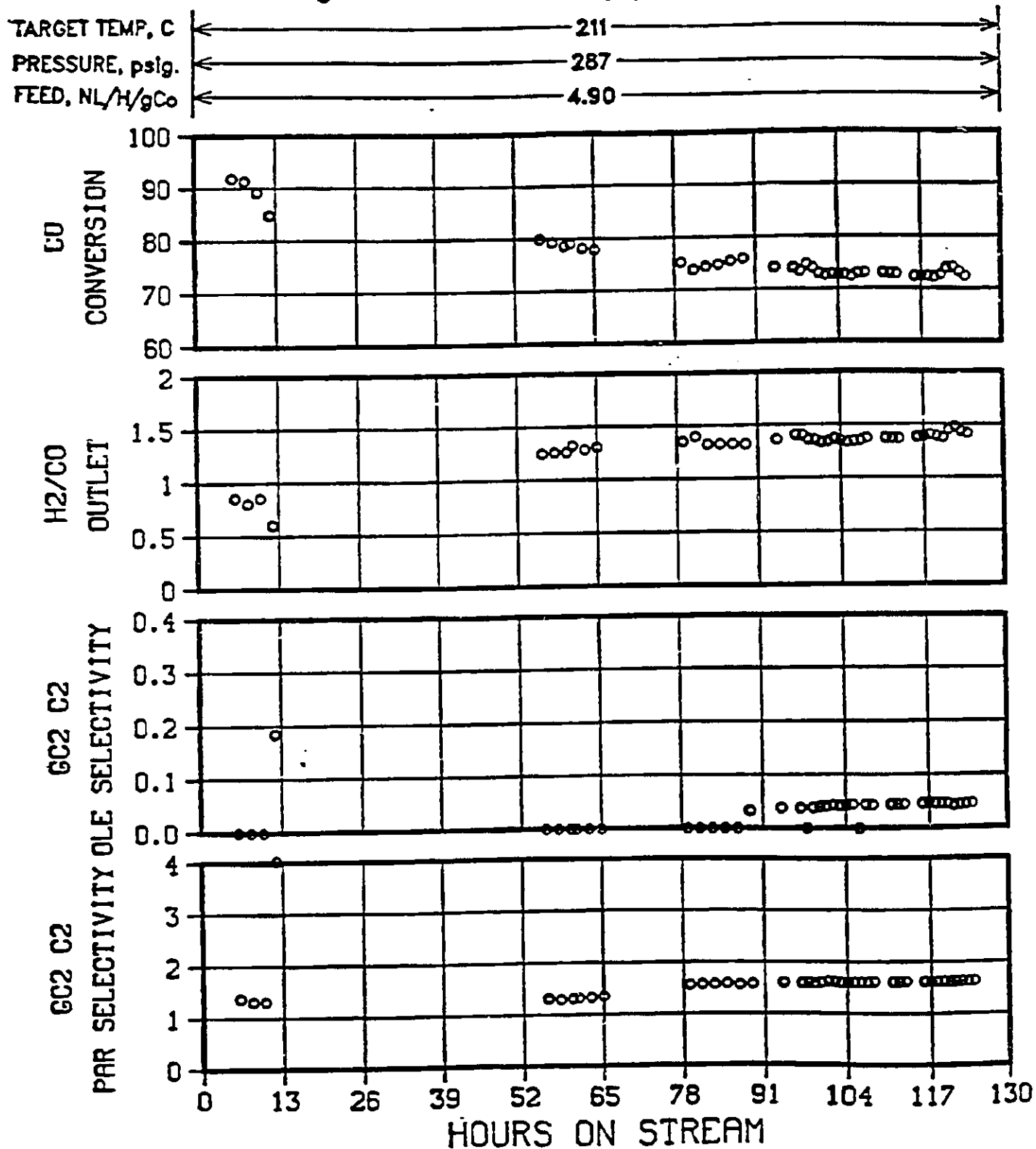


FIGURE A-6
PLT 700A RUN 97 Co, Mn, Zr, Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand

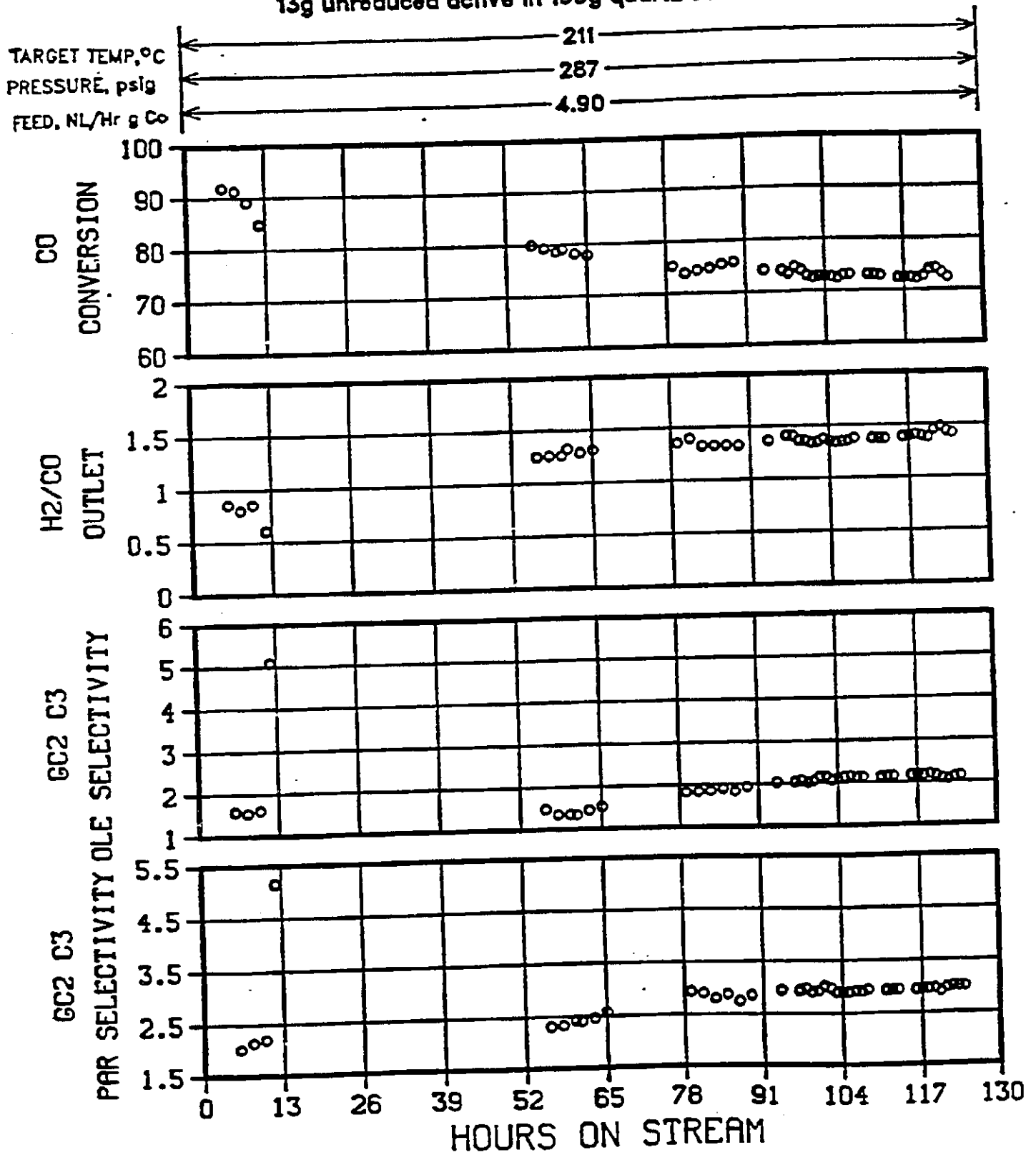
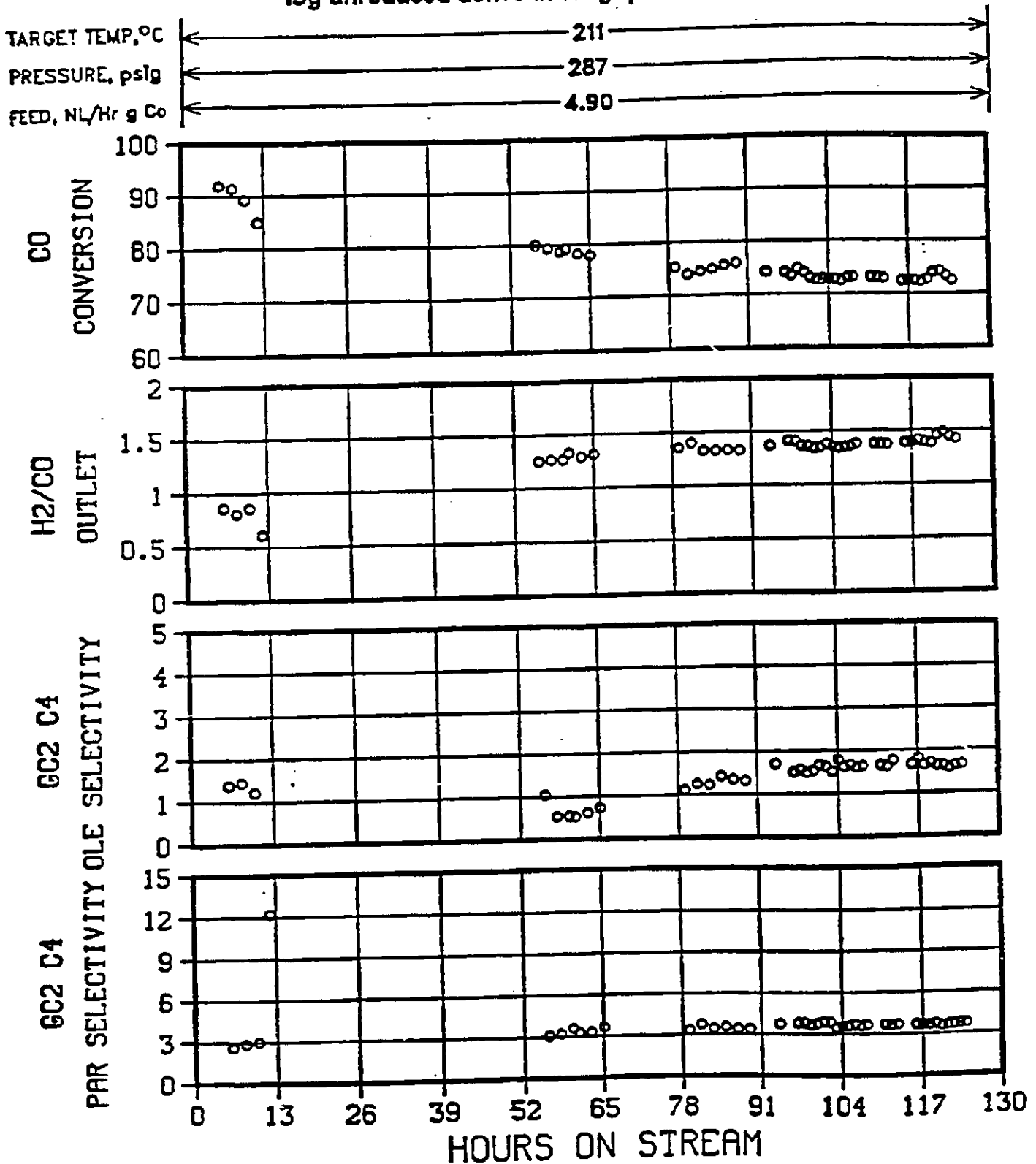


FIGURE A-7
PLT 700A RUN 97 Co, Mn, Zr, Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand



Temp Profiles RUN 97

FIGURE A-8

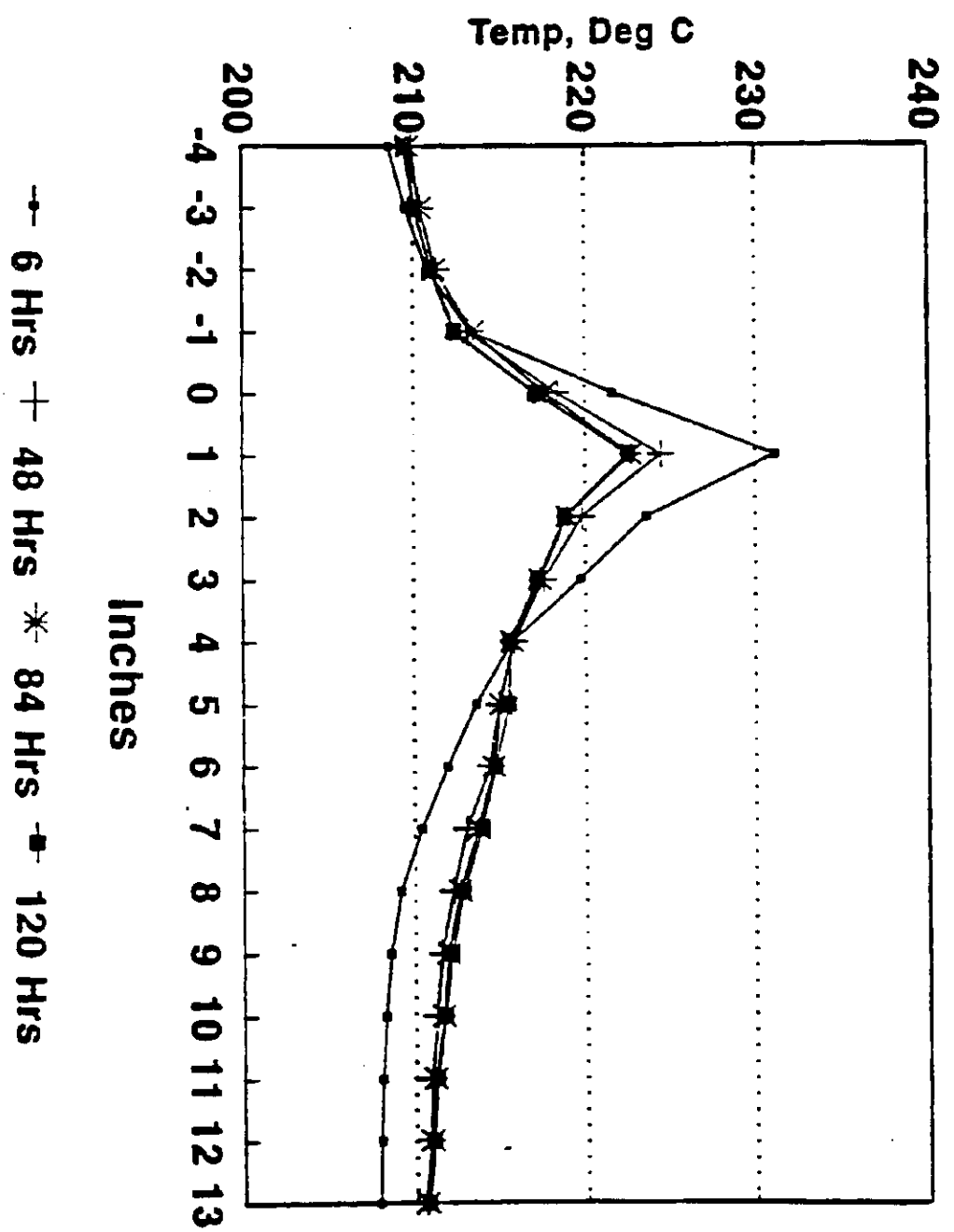


FIGURE A-9
PLT 700 RUN 104 Co, Mn, Zr, Ru on HCl Washed Y
6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H₂ Pretrt.
13g unreduced active in 160g quartz sand

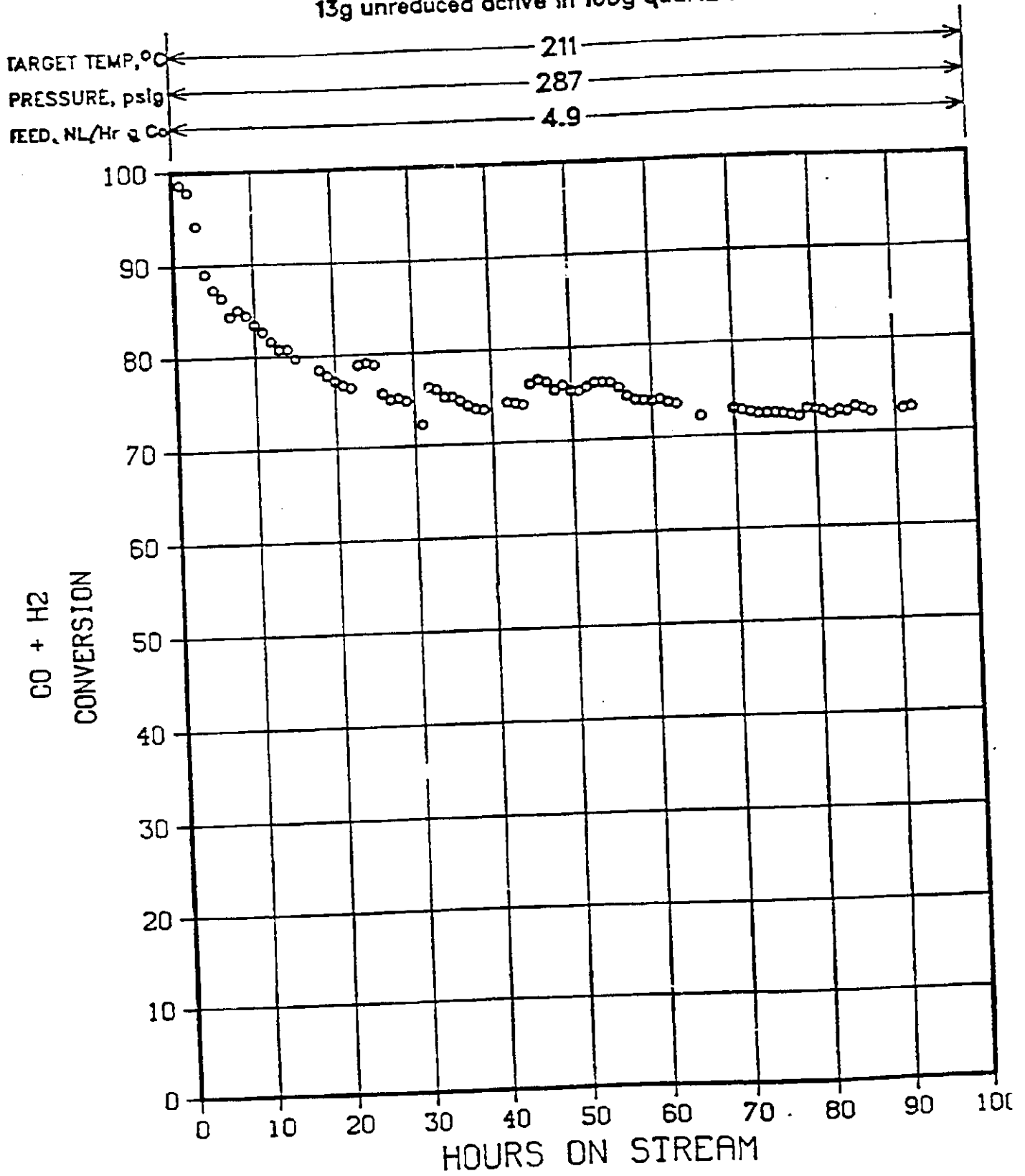


FIGURE A-10
PLT 700 RUN 104 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H2 Pretrt.
 13g unreduced active in 160g quartz sand

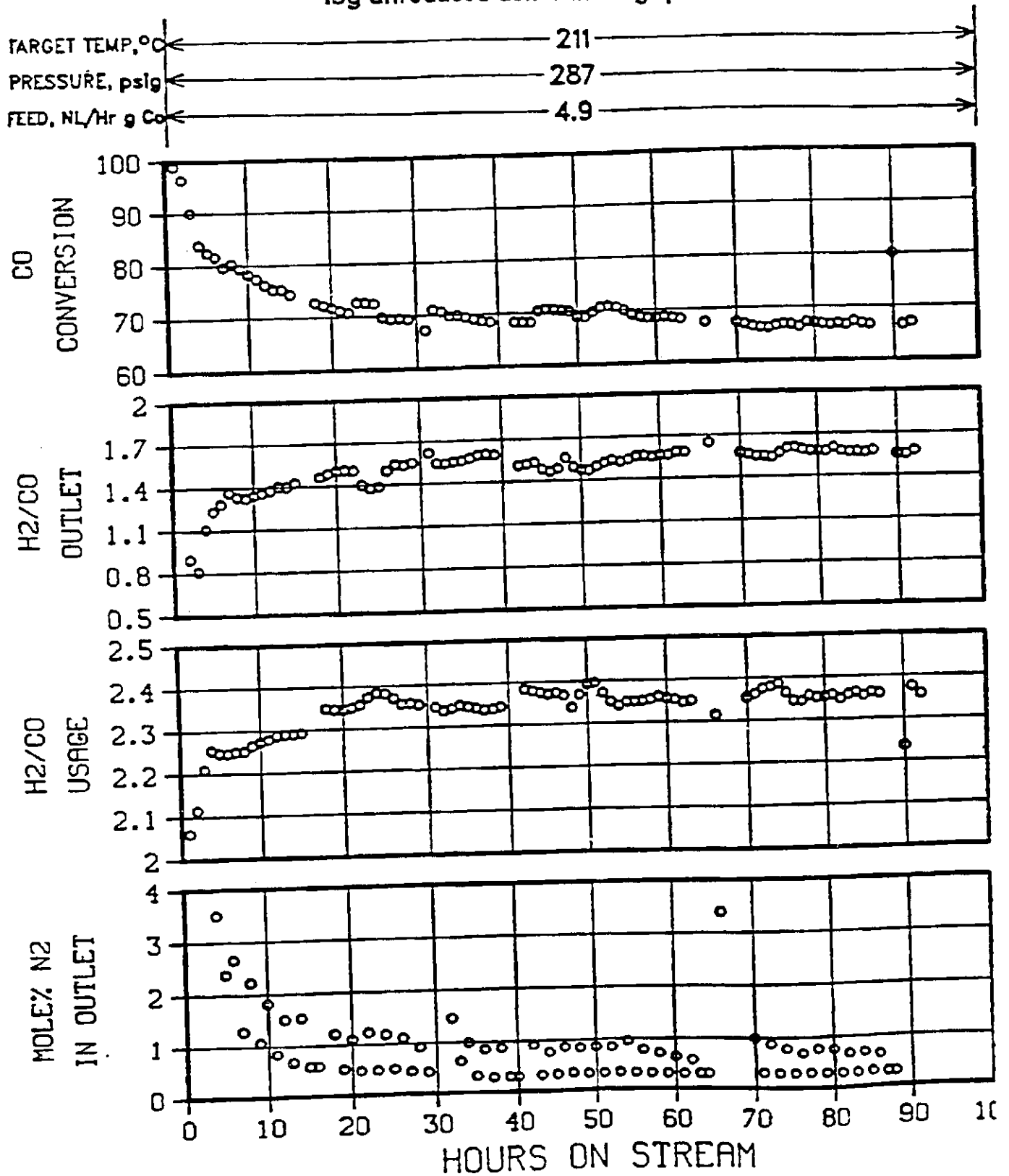


FIGURE A-11
PLT 700 RUN 104 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H2 Pretrt.
 13g unreduced active in 160g quartz sand

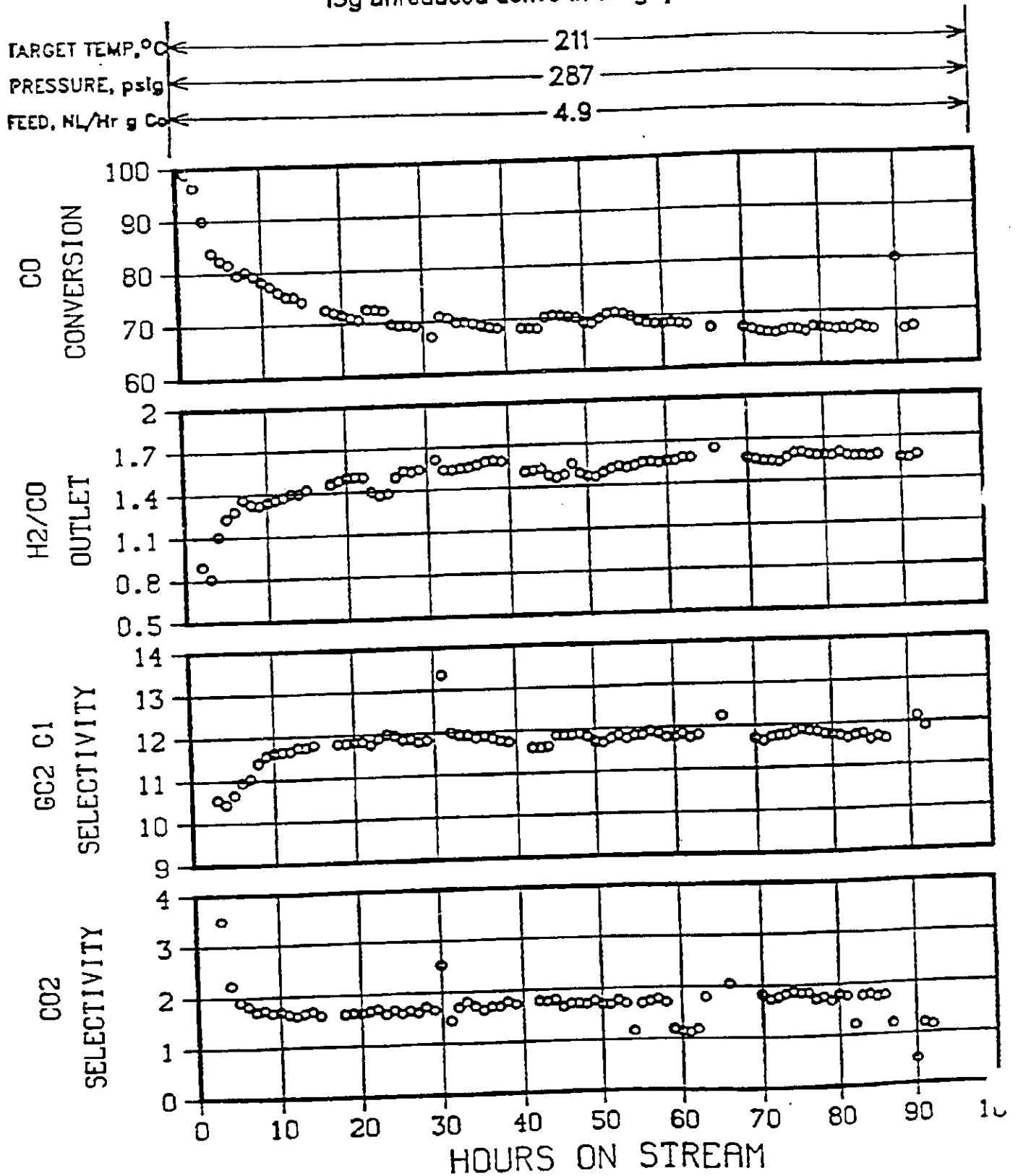


FIGURE A-12
PLT 700 RUN 104 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H₂ Pretrt.
 13g unreduced active In 160g quartz sand

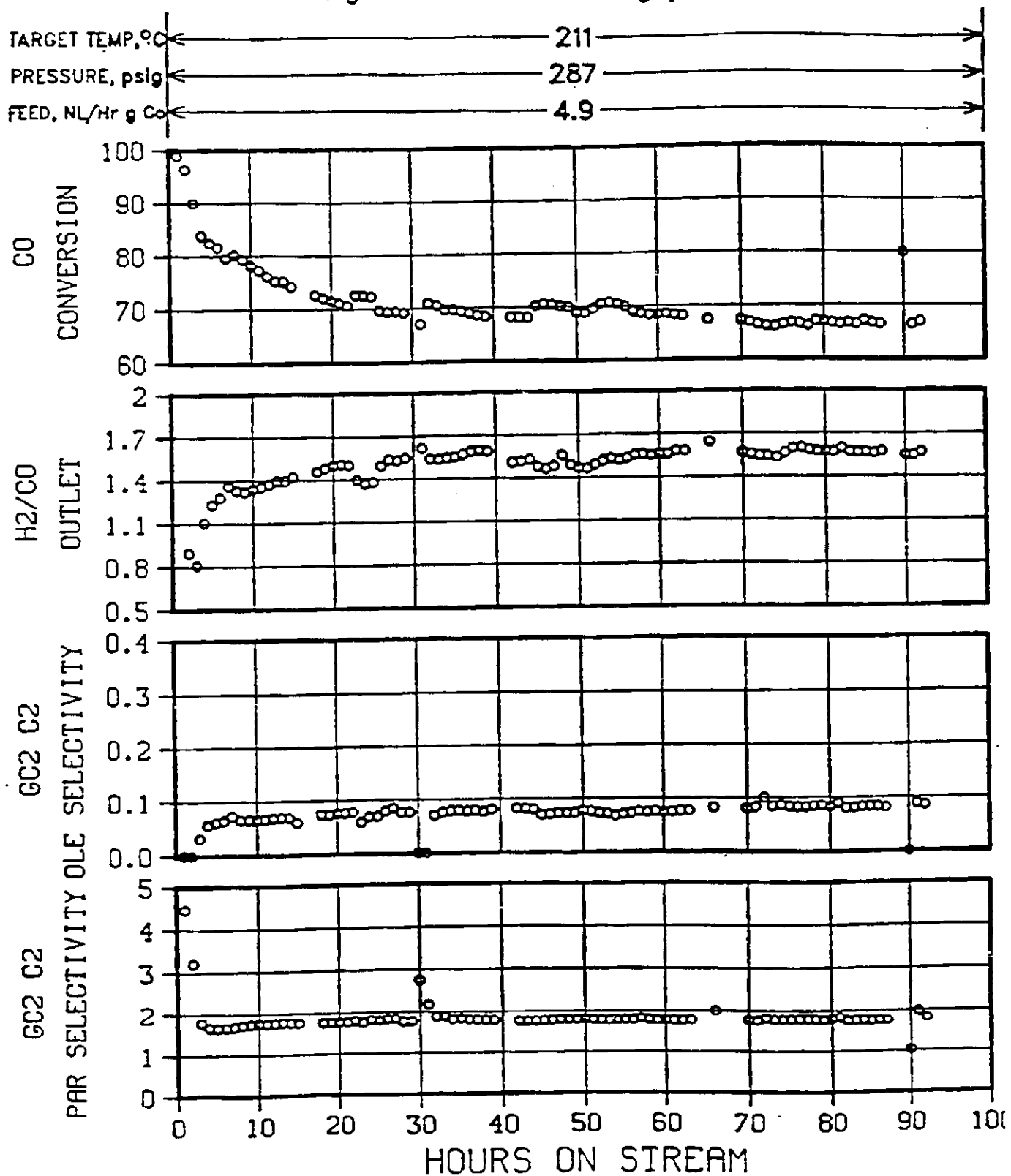


FIGURE A-13
PLT 700 RUN 104 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H₂ Pretrt.
 13g unreduced active in 160g quartz sand

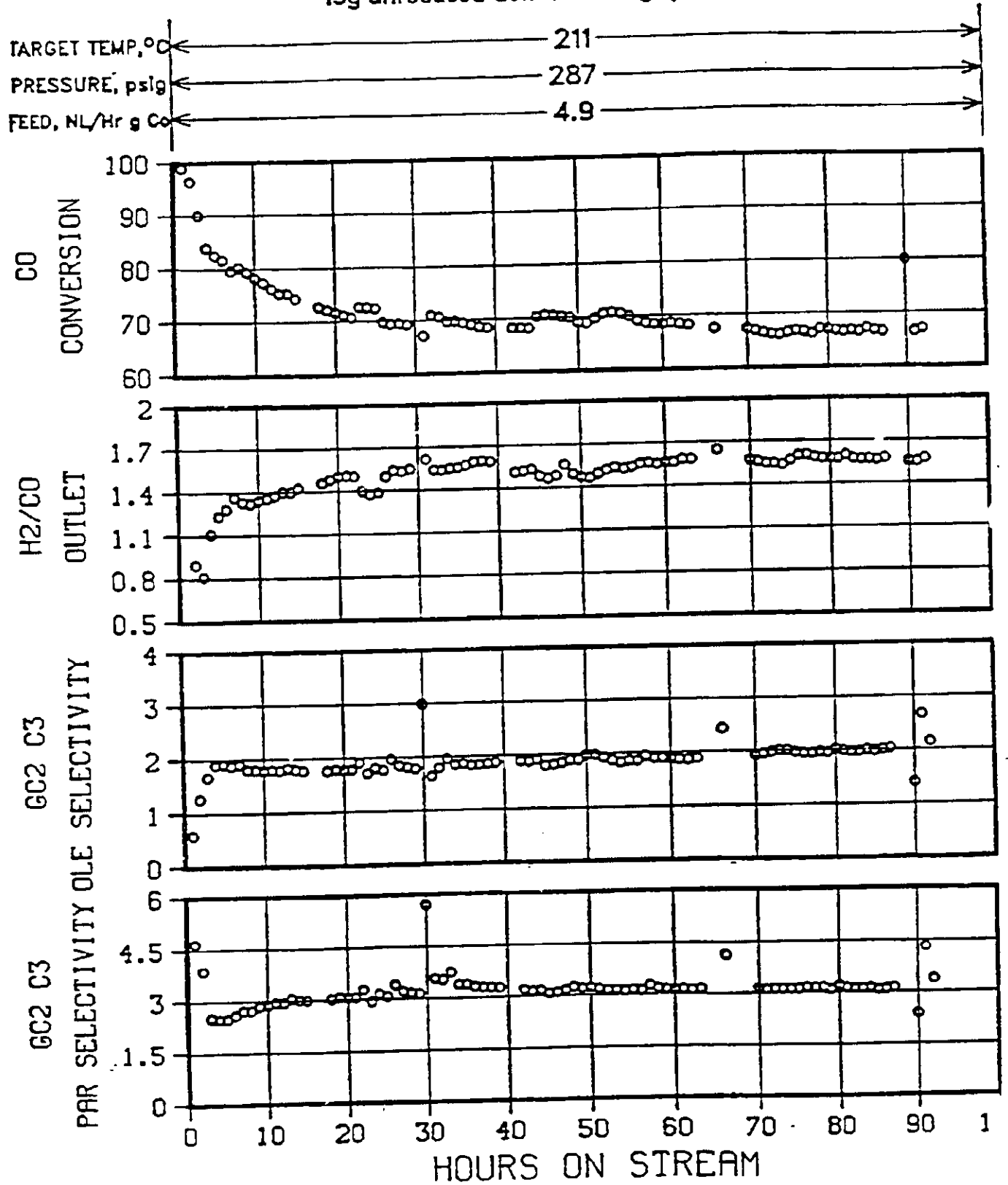
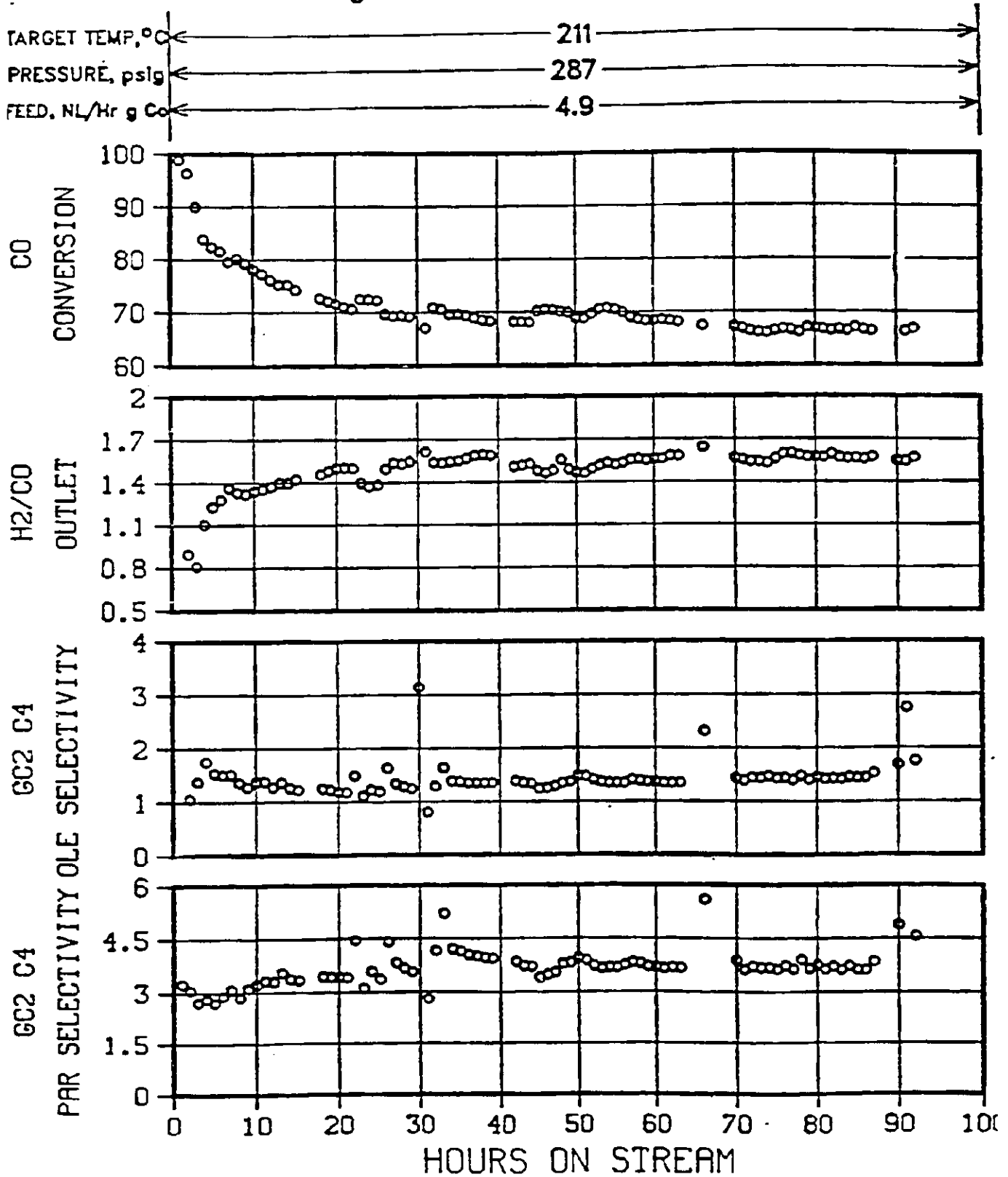


FIGURE A-14
PLT 700 RUN 104 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/325 C H2 Pretri.
 13g unreduced active in 160g quartz sand



**EFFECT OF REDUCTION CONDITIONS ON CATALYST PERFORMANCE
SUMMARY OF SCREENING IN FIXED-BED PLANT**

FIGURE A-15

RUN NO.	104	97	102
LOADING			
CATALYST, G		13	
DILUENT, G		160	
CATALYST PRETREAT.	325°/H ₂ /2 HRS	350°/H ₂ /2 HRS	375°/H ₂ /2 HRS
TEST CONDITIONS			
FEED H₂/CO		2.1	
FEED RATE (NL/H₂ · G C₀)		4.9	
TEMP, °C		211(INLET)	
PRESSURE, PSIG		287	
PERFORMANCE SUMMARY¹			
CONVERSION, %			
CO + H₂	72	78	49
CO	67	72	47
SELECTIVITY, MOLE %			
C₁	11.8	13	13
C₂	1.9	1.8	2.0
C₃⁻	0.1	0.1	0.2
C₃	3.1	3.0	3.5
C₃⁻	2.0	2.1	2.7
CO₂	1.8	0.8	1.0

1. AT 100 HOURS ON STREAM

FIGURE A-16
 PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H2 Pretrt
 13g unreduced active in 160g quartz sand

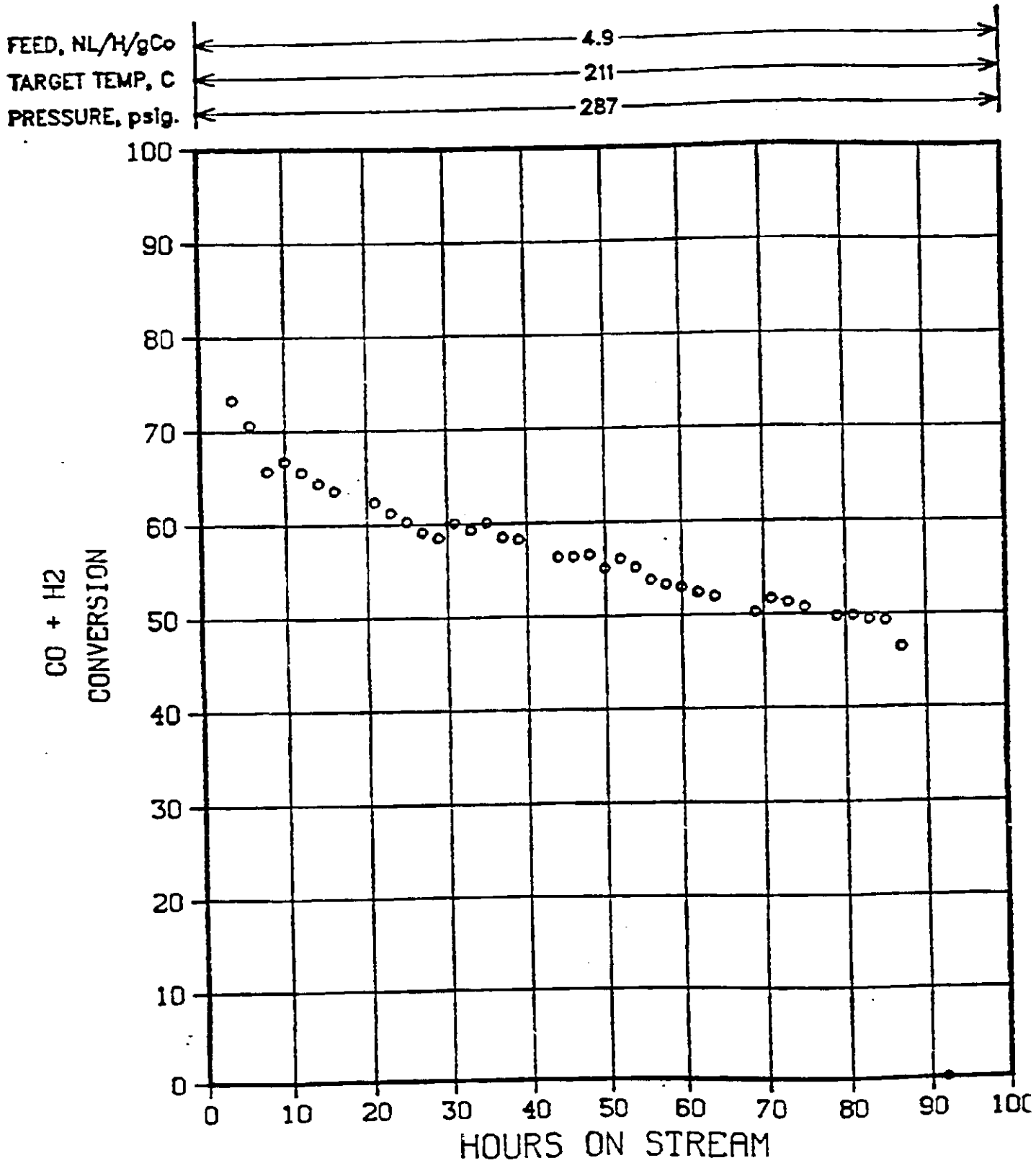


FIGURE A-17
PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H2 Pretrt
 13g unreduced active in 160g quartz sand

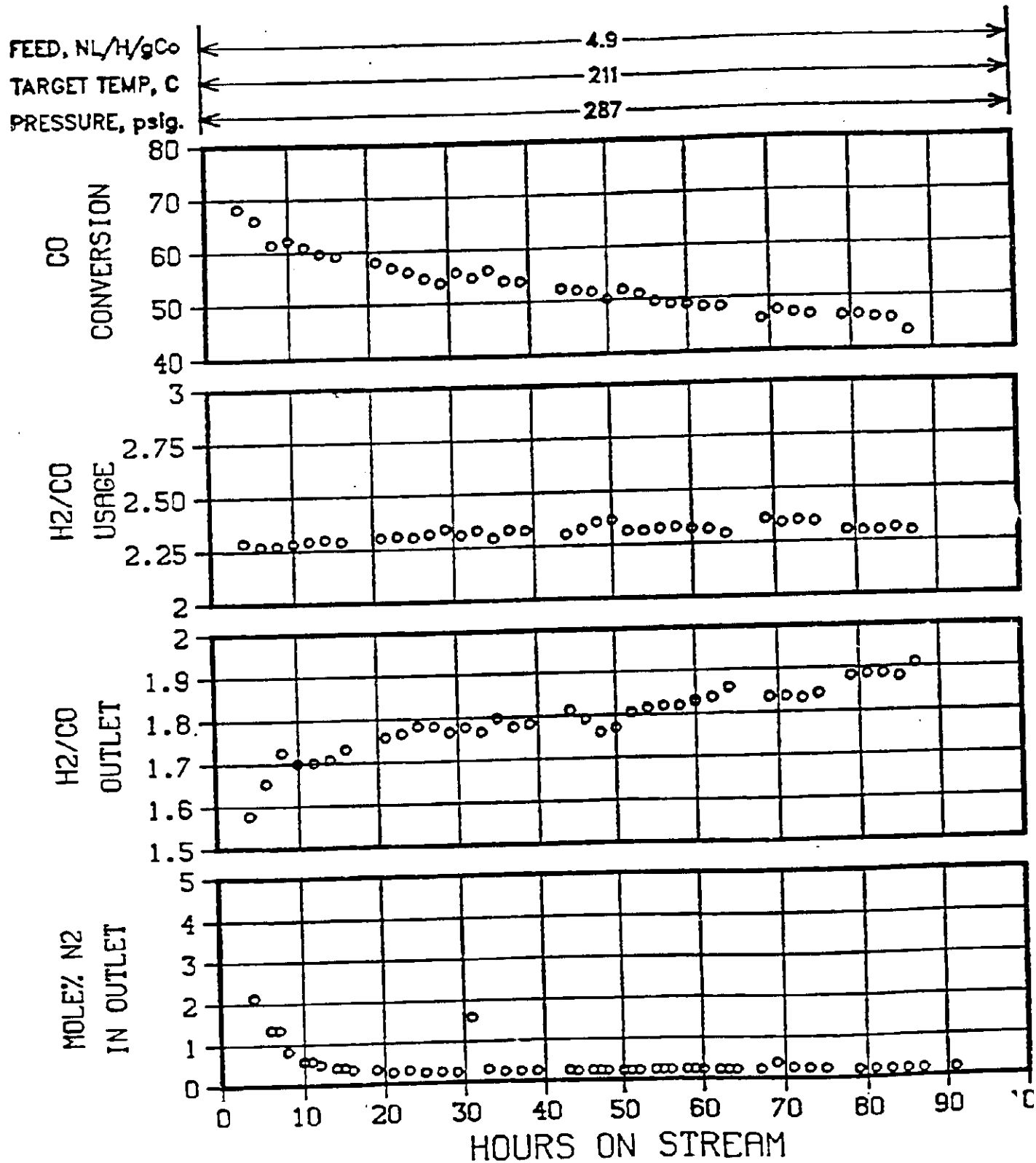


FIGURE A-18
PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H2 Prett
 13g unreduced active in 160g quartz sand

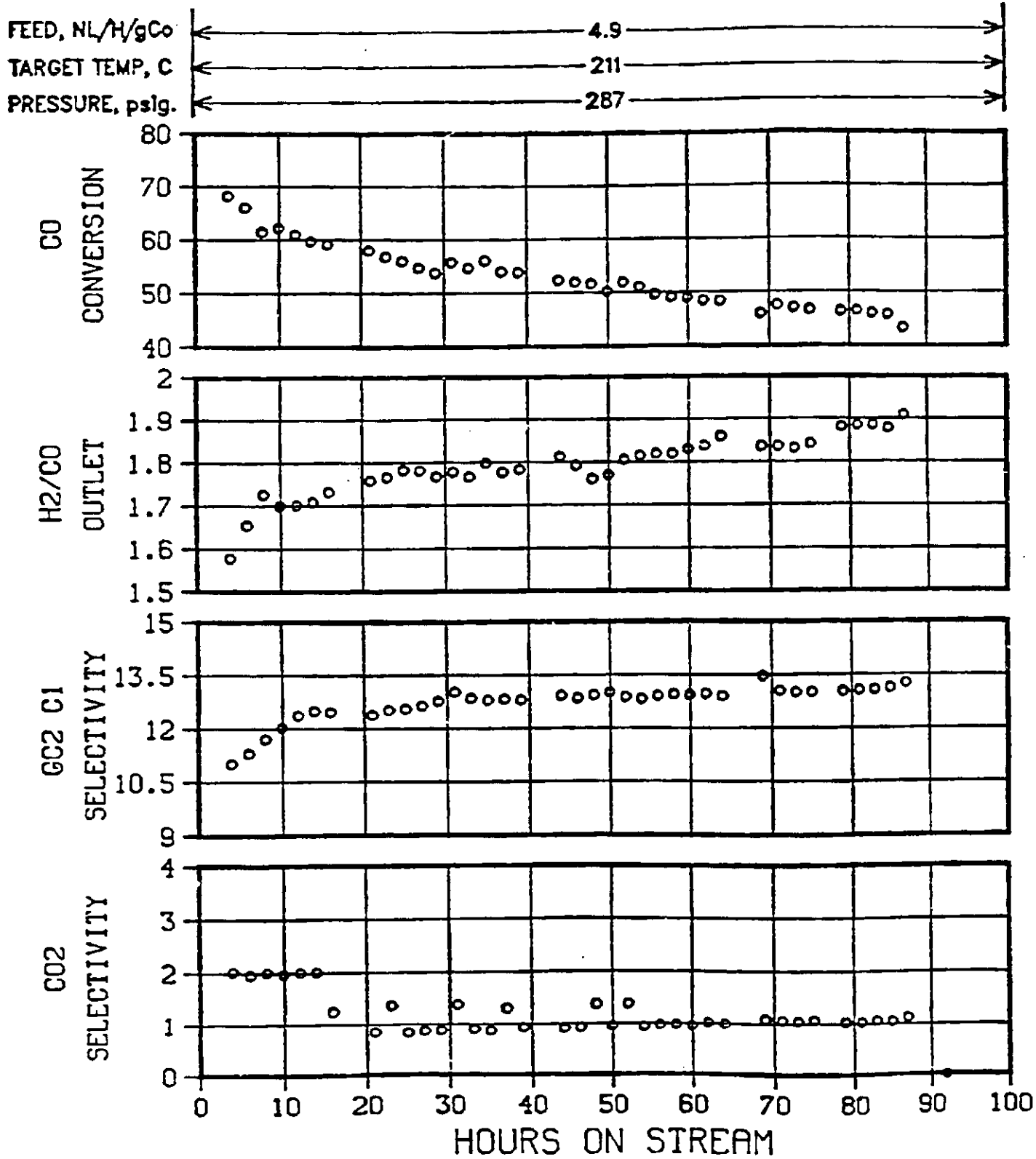


FIGURE A-19
PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H₂ Pretrt
 13g unreduced active In 160g quartz sand

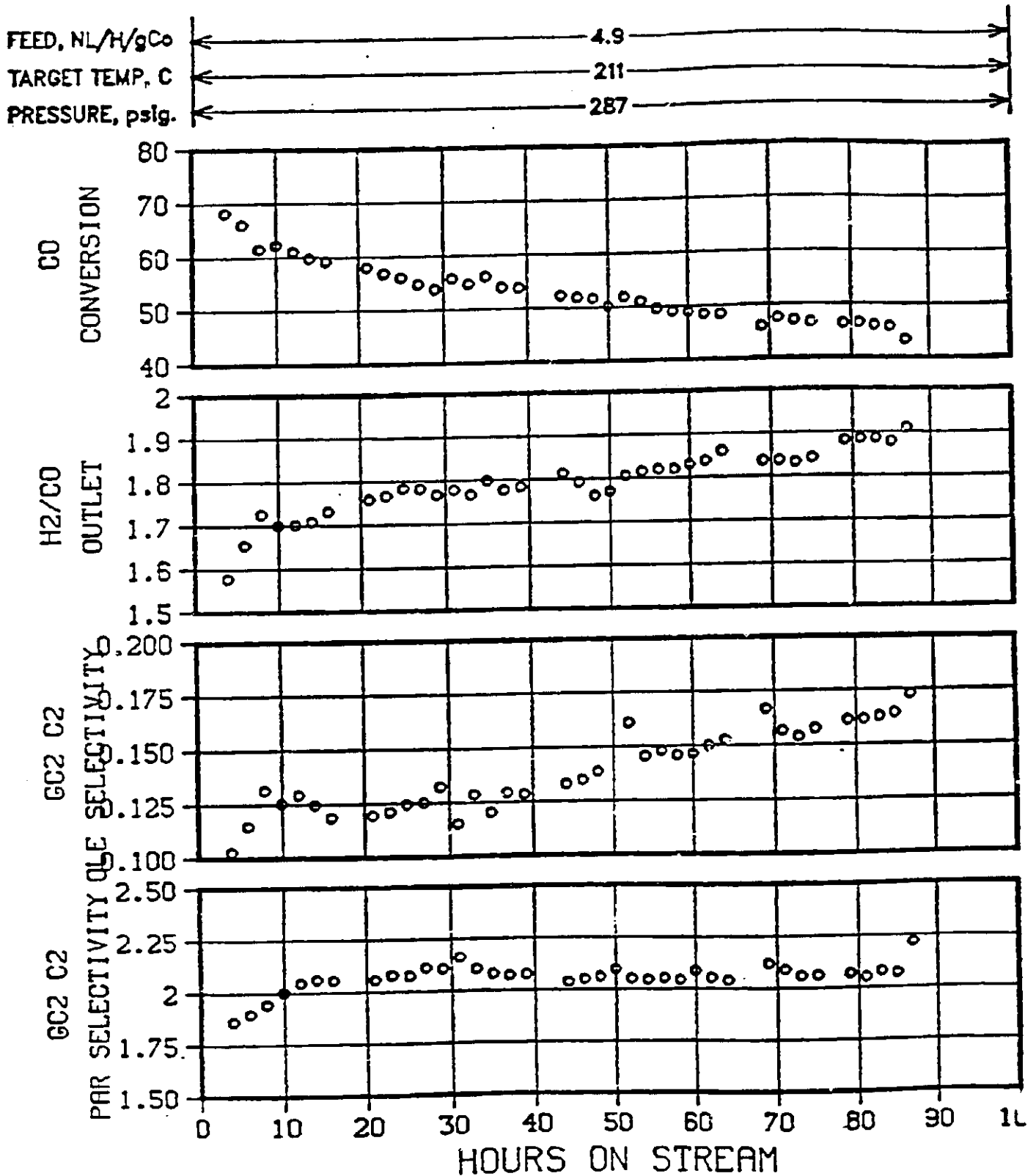


FIGURE A-20
PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H2 Pretrt
 13g unreduced active in 160g quartz sand

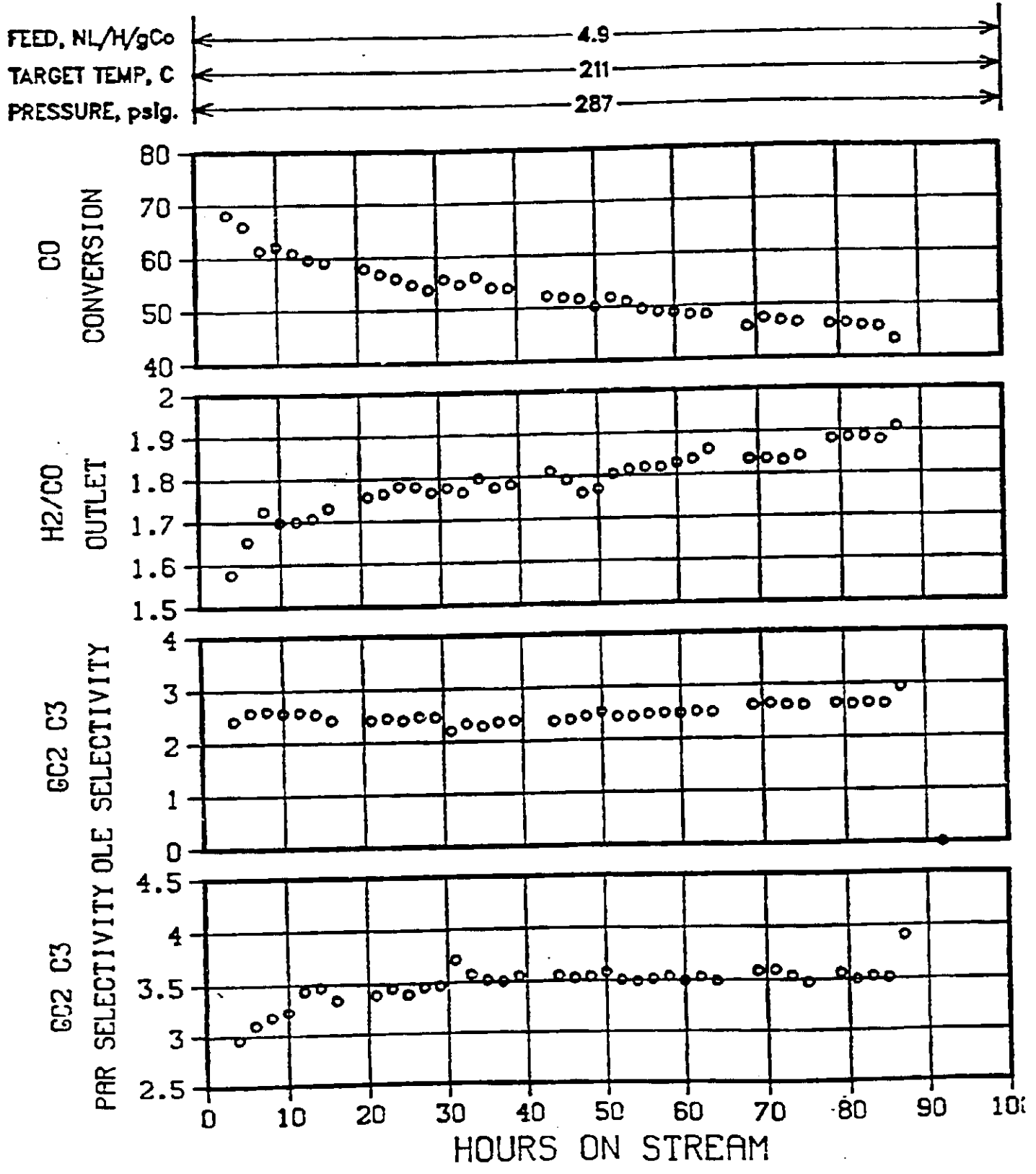


FIGURE A-21
PLT 700 RUN 102 Co,Mn,Zr,Ru on HCl Washed Y
 6827-99 w/18.5 % Co via eth-glycol pore fill/375 C H2 Pretrt
 13g unreduced active in 160g quartz sand

