DOE/PC/90055--T1

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

DOE/PC/90055--T1

DE92 005264

Contract DE-AC22-90PC90055

UOP
25 E. Algonquin Road
Des Plaines, Illinois

Technical Progress Report No. 2
(12/26/90 - 3/26/91)

CONTRACT OBJECTIVE

The objectives of this contract are to develop a technology for the production of active and stable iron 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 H_2 and CO in the molar ratio of 0.5 to 1.0, the catalyst performance target in the slurry bubble-column reactor 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 THE WORK DURING THE REPORTING PERIOD

A total of four runs was made in the slurry autoclave plant during this period. Experiments were begun to determine the reproducibility of the catalyst testing procedure under Task 2.0. Enough of catalyst 752R16B5C was available for three runs (Runs 24 to 26), which were to be run at the same operating conditions. However, because of operational difficulties, the catalyst pretreatment procedure was not the same in the second run (Run 25). As a result, catalyst performance during these two runs (24 and 25) was not the same. The effect of pretreatment on catalyst performance is planned to be investigated under Task 1.4. Because three runs under identical conditions were not possible, the final one-third of the catalyst was used to determine how a change in the operating pressure during a run will affect conversion and selectivity.

The fourth run during this reporting period was made with Catalyst 752R17B2A. This run was carried out at the lower pressure of 290 psig.

TASK 2.0

Four different runs (Runs 24 to 27) were conducted in the slurry autoclave pilot plant. The catalyst testing procedure and conversion-selectivity calculations were described in the technical progress report covering the period from 4/1/90 to 6/30/90 of the previous Contract DE-AC22-87PC79812. The catalytic performance in these four runs are compiled in the appendix. The specific test conditions used are indicated in these performance data summaries.

In all runs, 72.7 g of catalyst were loaded with 290 g of a C_{30} oil obtained from the Ethyl Corporation. The catalyst was activated in the presence of a feed mixture containing H_2 and CO in the molar ratio of 0.7. Unless otherwise noted, the pretreatment consisted of 12 hr with 2 NL/hr/gFe at 280°C and 153 psig. During the remainder of the run, the feed rate was increased to 2.4 NL/hr/gFe, and temperature was lowered to 265°C. The pressure was not always the same during a run.

Run 24

Precipitated iron catalyst 752R16B5C was evaluated over a 320-hr period. After the first 18 hr, the pressure was increased to 500 psig. This Fe-Cu catalyst was from the same catalyst preparation run that furnished the catalyst for Runs 20 to 23 (see Technical Progress Report No. 1). The $CO+H_2$ conversion fell from 85% at 20 hr to 61% at 320 hr. The methane and ethane selectivities increased throughout the run, but the rate of increase at the end of the run was very low. At 320 hr, the sum of the methane and ethane selectivities was 5.5%. The selectivity of CO to CO_2 was about 47%, indicating substantial water gas shift activity.

Run 25

A fresh sample of the catalyst 752R16B5C was used in this run. The intention was to exactly duplicate Run 24 to determine the reproducibility of the catalyst testing procedure. However, inadvertent changes were made to the catalyst pretreatment procedure (Table 1).

TABLE 1

CATALYST PRETREATMENT CONDITIONS

	Hours on-Stream	
	Run 24	Run 25
Time at 280°C	0 to 12	0 to 12
Time to go from 280 to 265°C	12 to 15	12 to 15
Time to go from 153 to 300 psig	15 to 18	24 to 25
Time when feed rate changed from 2.0 to 2.4 NL/hr/gFe	15	25

This run was carried out for 178 hr. The $CO+H_2$ conversion fell from 81% at 25 hr to 78% at 178 hr. Over the same period, the $CO+H_2$ conversion in Run 24 fell from 85 to 69%. From this limited data, determining whether this difference in the rate of catalyst deactivation is due to run-to-run variation or to the different pretreatment conditions is not possible. Work to be carried out under Task 1.4, Catalyst Pretreatment, will help address this issue. Task 1.4 is

scheduled to begin in January 1992. At 178 hr, the sum of methane and ethane selectivities was 6.2%. The selectivity of CO to CO_2 was similar to that in Run 24.

Run 26

This run was also carried out with catalyst 752R16B5C. Catalyst pretreatment and all the operating conditions, except pressure, were the same as in Run 25. The pressure during the run was 290 psig, which was down from the 500 psig maintained in Runs 24 and 25. The conversion, after catalyst pretreatment, was lower than that obtained in Run 25. At 63 hr of on-stream time, the operating pressure was increased to 500 psig. This increase resulted in a conversion level similar to that obtained during Run 25 just after catalyst pretreatment. The pressure change also caused an increase in both methane and ethane selectivities, which appeared to be lining out at 4.4% and 1.6% respectively at the end of the run (120 hr). These observed increases in methane and ethane selectivities may be partly explained by the increase in the H_2:CO molar ratio at the higher conversion level. The selectivity of CO to CO_2 was similar to that observed in Runs 24 and 25.

Run 27

A fresh sample of another catalyst (752R17B5A) was used with the same catalyst pretreatment procedure as in Runs 25 and 26. After catalyst pretreatment, the operating conditions were the same as in Run 26. The one difference was that the operating pressure was maintained at 290 psig throughout the run. The CO+H_2 conversion just after catalyst conditioning (30 hr) was 70%, which is essentially the same as the 71% conversion at 30 hr observed in Run 26. This run lasted for 115 hr. At the end of the run, the methane and ethane selectivities appeared to be approaching line out at 4.6% and 1.6%, respectively. The selectivity of CO to CO_2 was similar to Runs 24, 25, and 26.

CONCLUSIONS

The methane and ethane selectivities were low at the beginning of a run (during and after catalyst activation). However, these selectivities rapidly increased and appeared to approach

line out near the end of the longest run (320 hr in Run 24). Understanding the chemical nature of the fresh catalyst when it is producing low levels of methane and ethane is one of the goals of this project.

The run-to-run reproducibility in the pilot plant has not yet been assessed. Demonstration of run-to-run reproducibility remains a high-priority item and will be accomplished by the end of the next quarter.

For catalyst 752R16B5C (Run 26), an increase in plant pressure from 290 to 500 psig was found to cause an increase in CO conversion by 10% (from 75 to 85%). However, this increase was accompanied by increases in methane and ethane selectivities.

The catalyst used in Run 27 (752R17B5A) was from a different lot than that used in the other runs but was similar in behavior. For instance, Run 27 can be directly compared to Run 26 up to 63 hr because the activation procedures and run conditions were the same until then. At 63 hr, Run 27 CO conversion was 71% vs. 75% for Run 26. The methane and ethane selectivities in Run 27 were, respectively, 4.5 % and 1.4% vs. 3.8% and 1.4% for Run 26.

APPENDIX

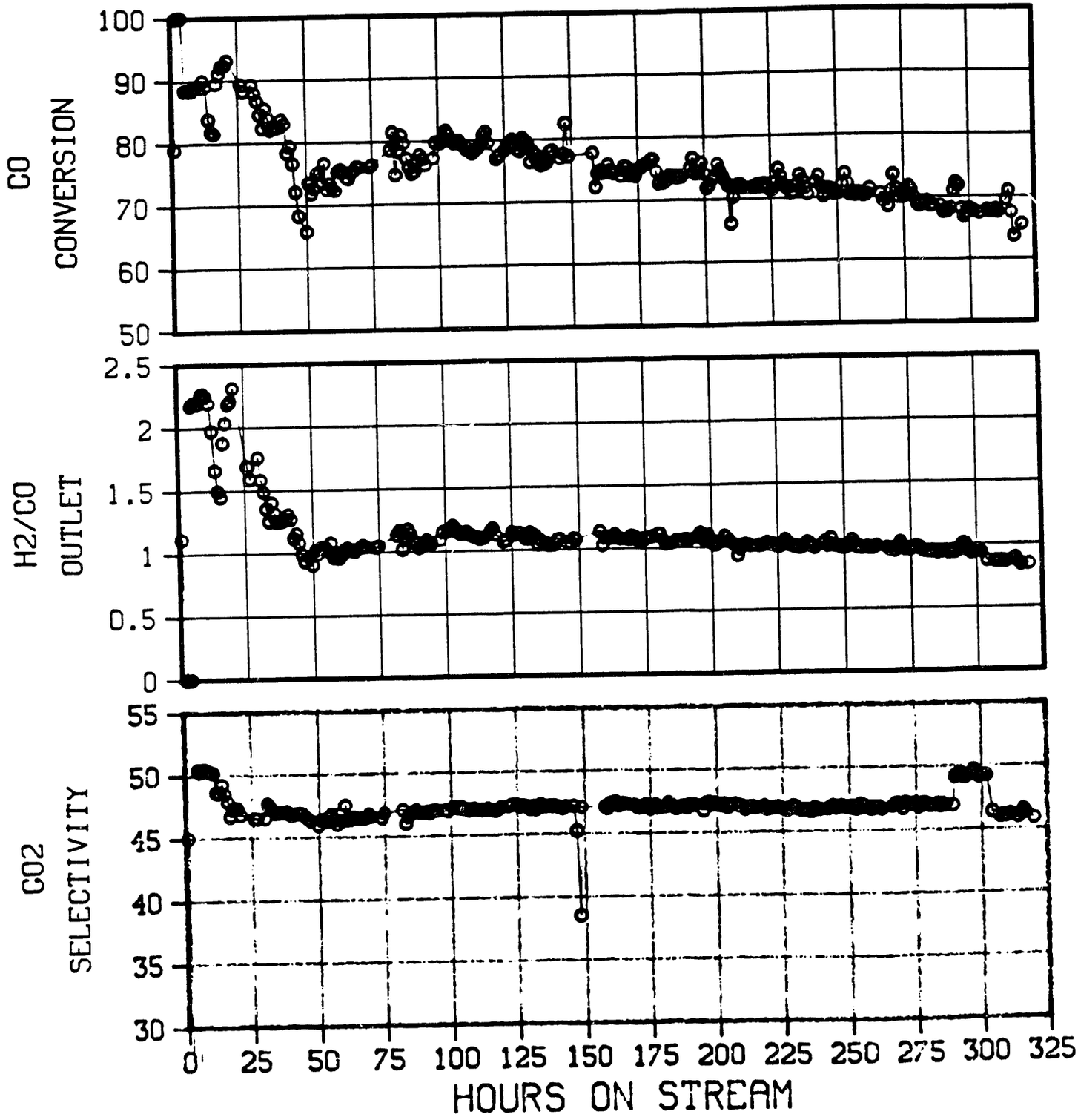
SUMMARY OF RUNS 24-27, PLANT 700B

PRECIPITATED IRON CATALYST 6616–37 IN SLURRY AUTOCLAVE

RUN 24, PLT 700B H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R16B234 **72.7g cat, 290g C_{30} oil**

TARGET TEMP, C	280	265
PRESSURE, PSIG	153	500
FEED, NL/H g Fe	2.0	2.4



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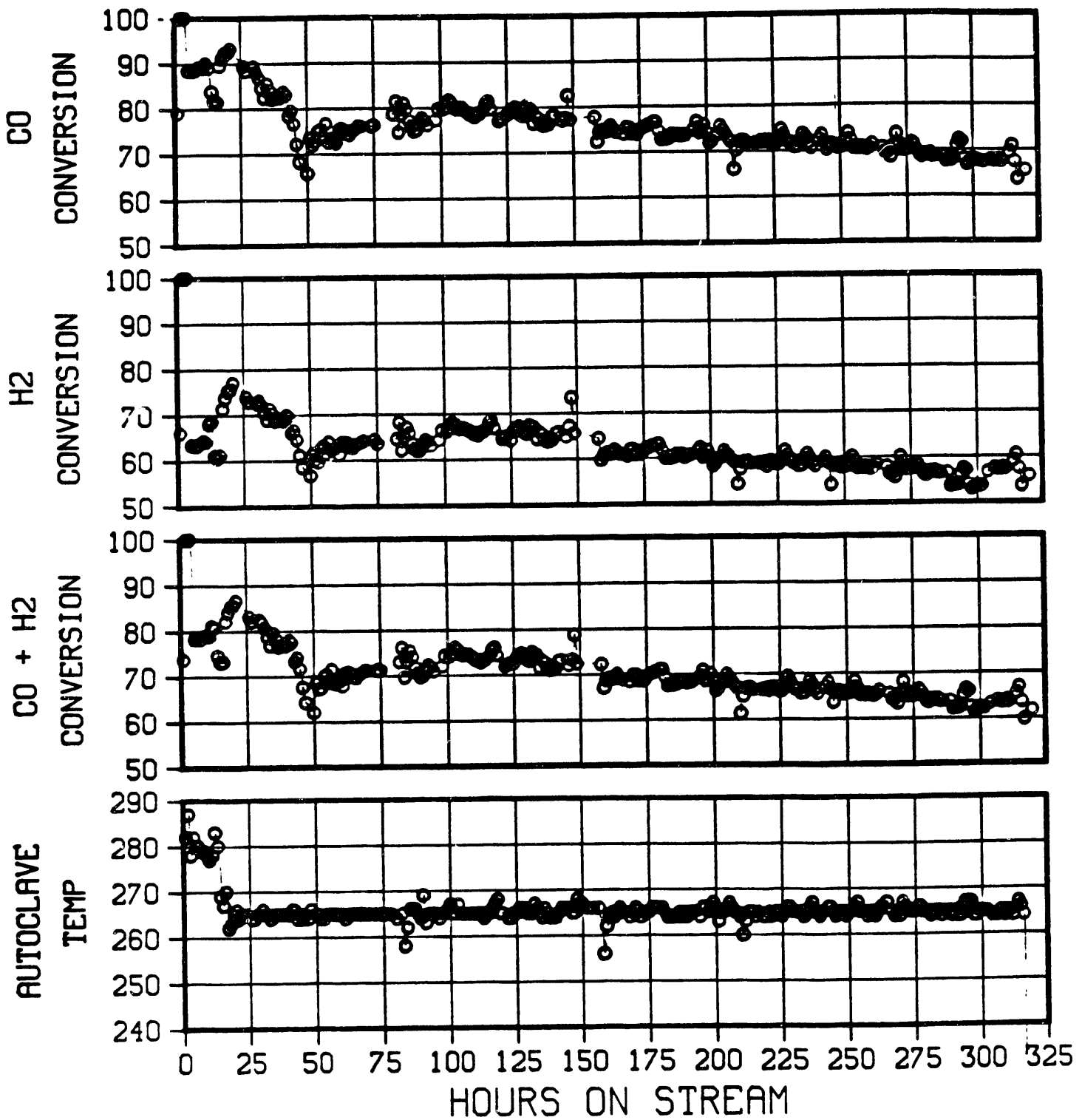

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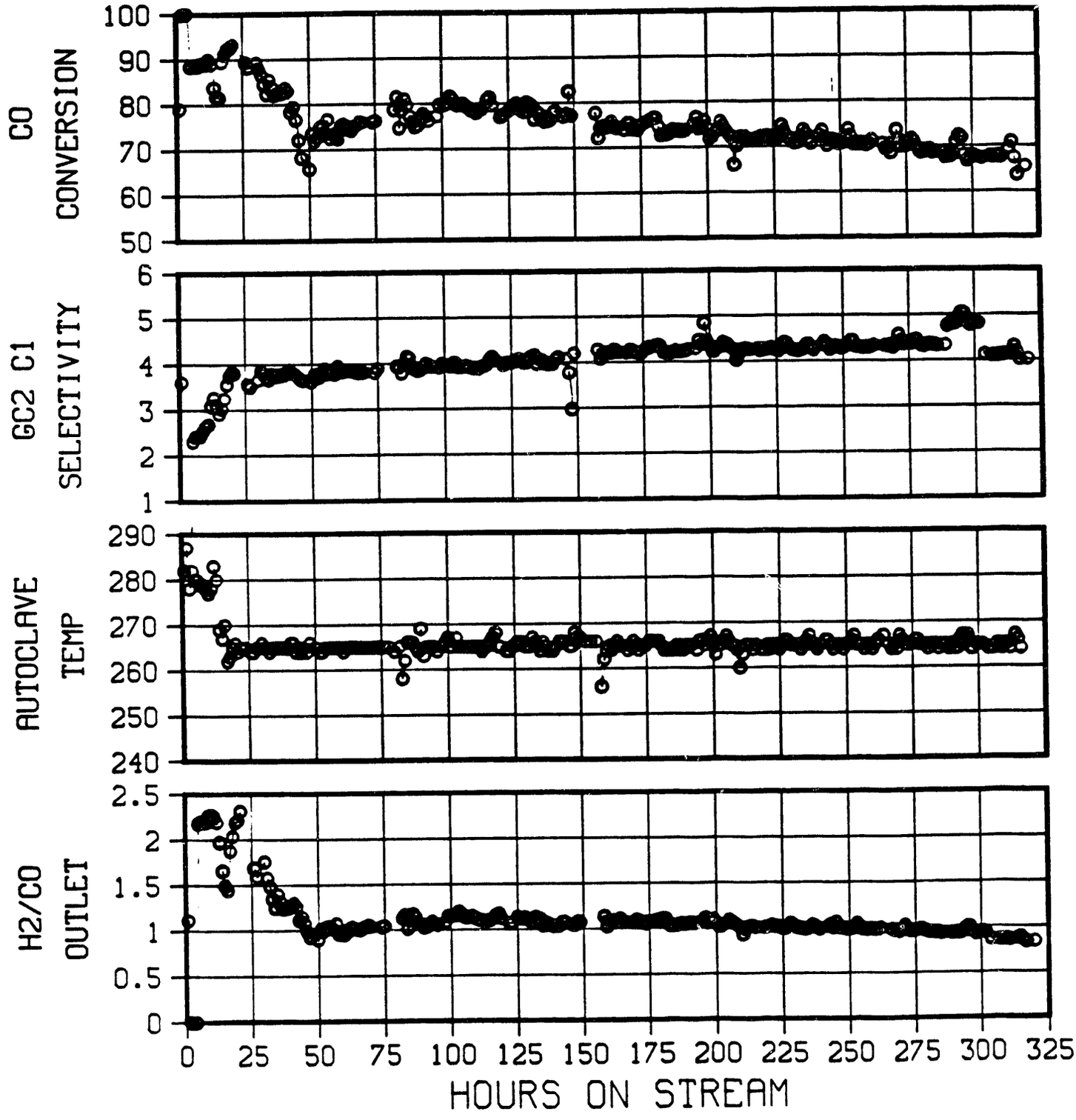

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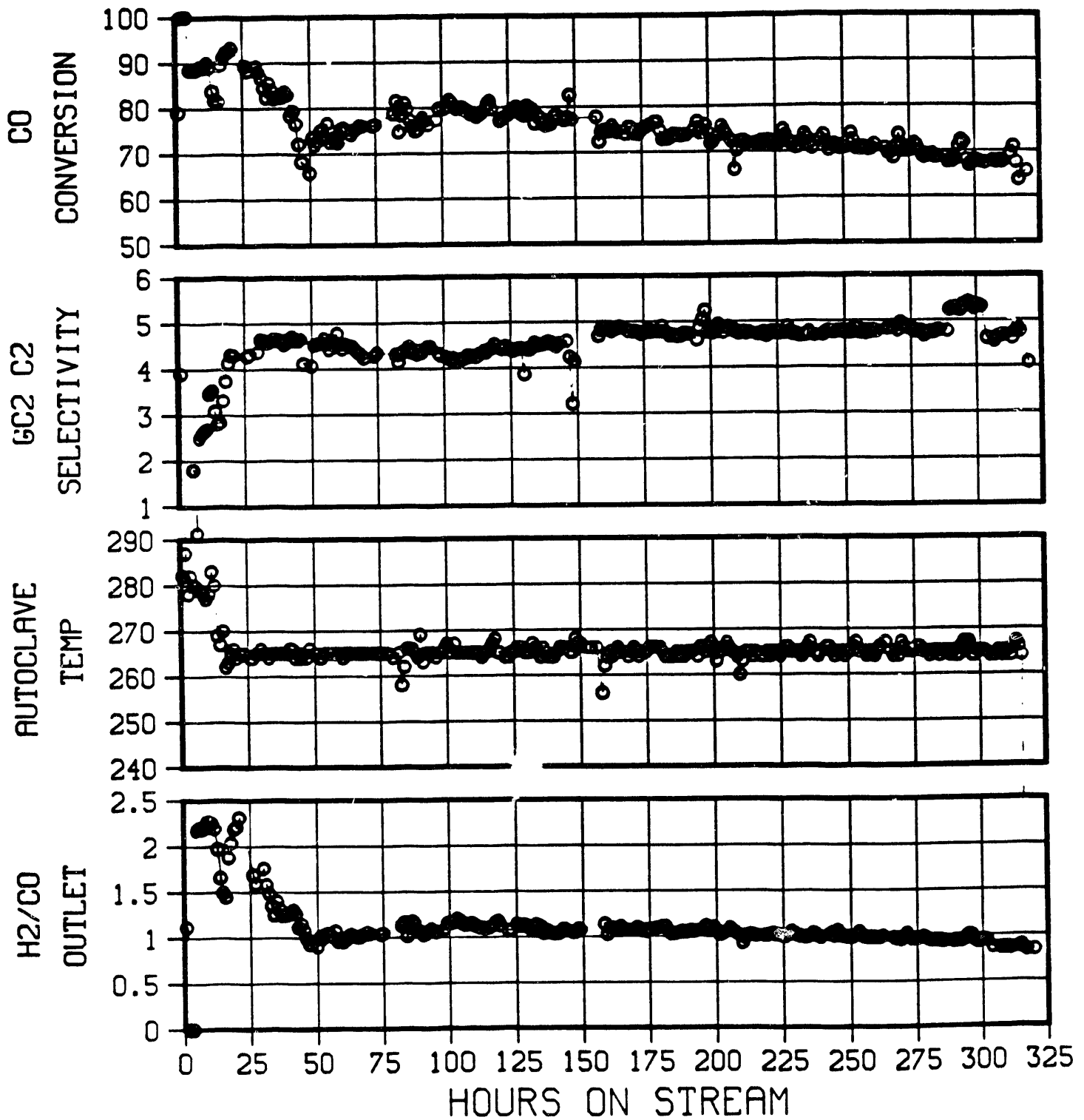

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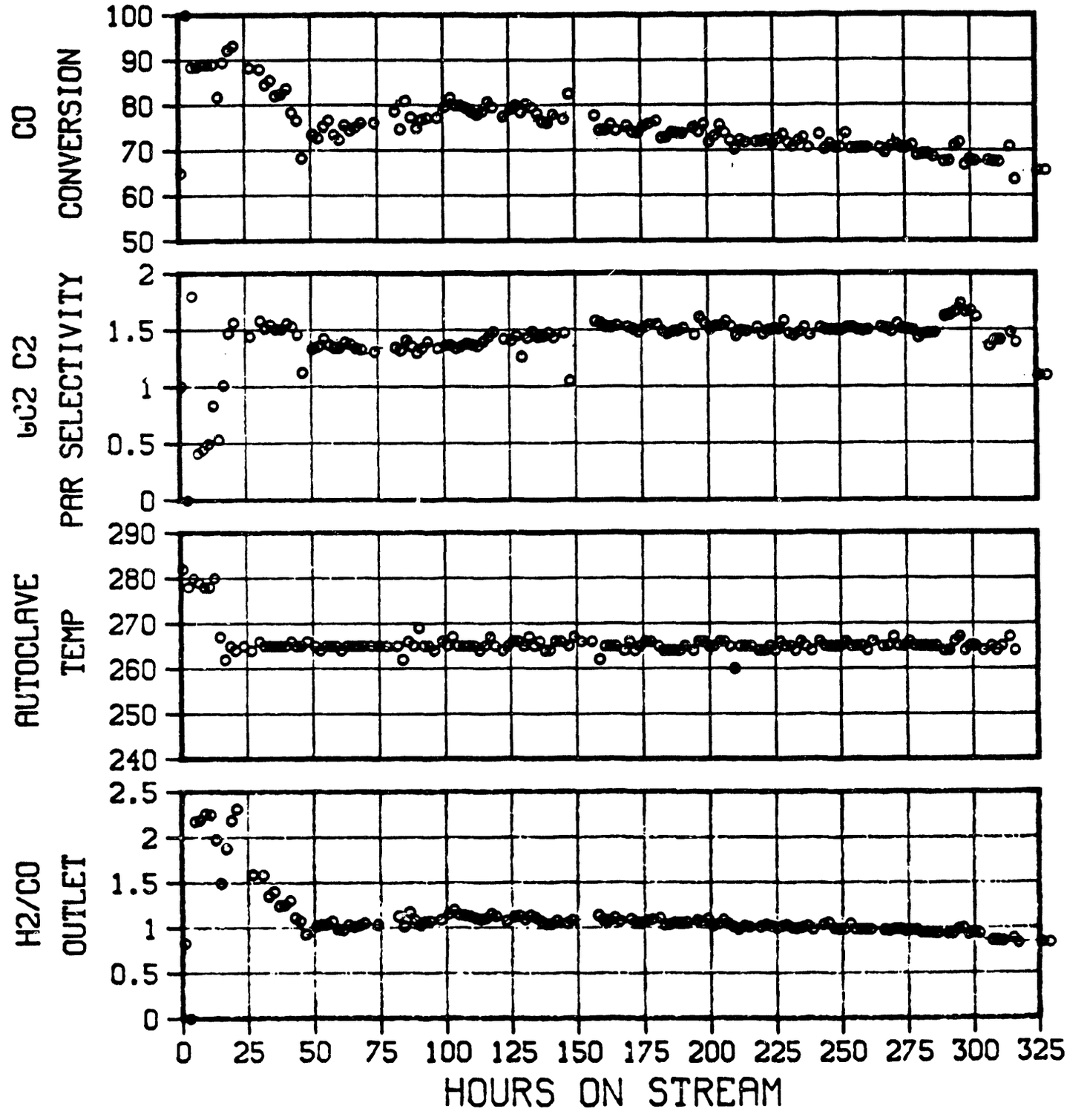
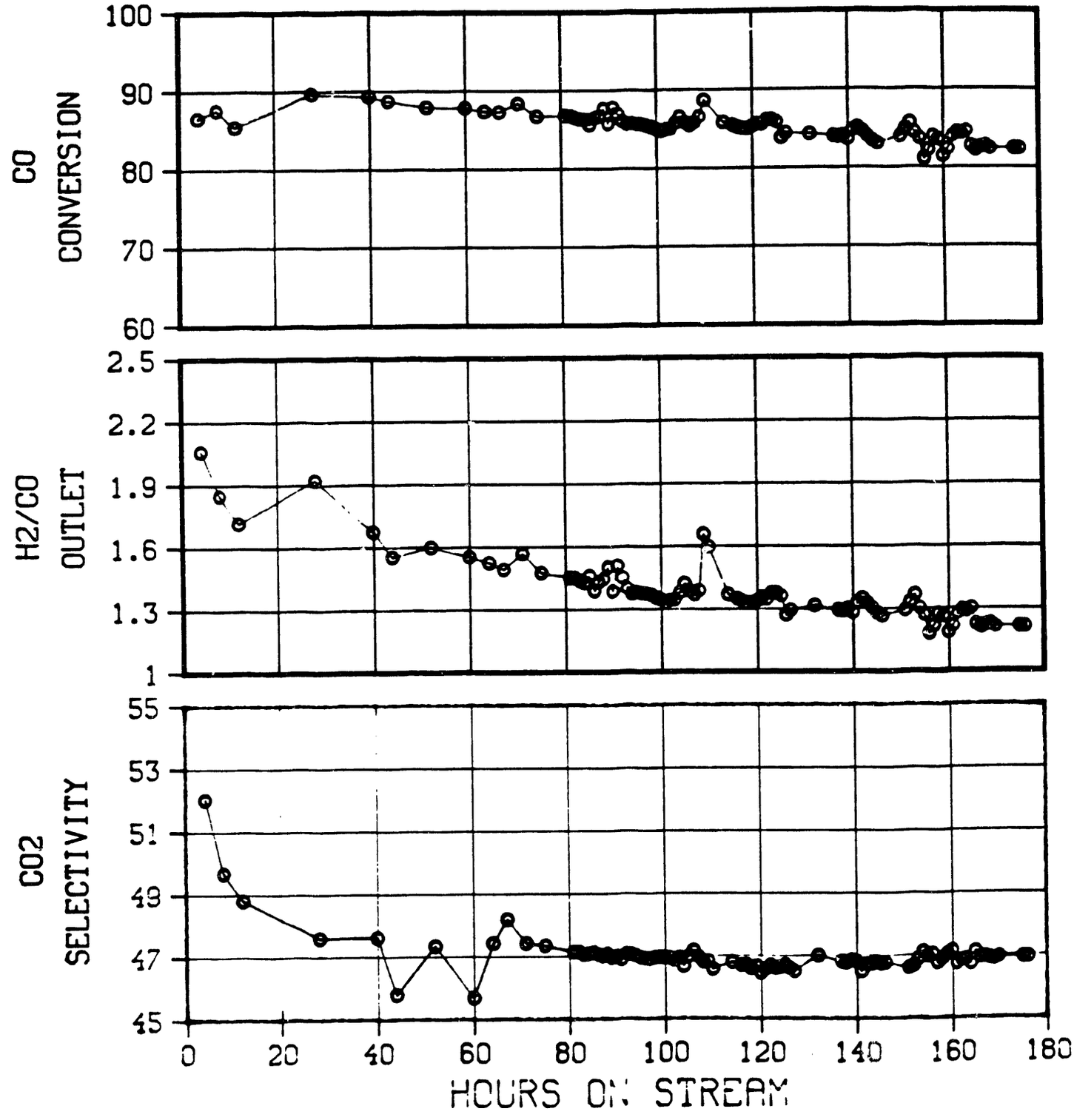


PRECIPITATED IRON CATALYST 6616–37 IN SLURRY AUTOCLAVE

PLT 700B RUN 25 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R16B234 72.7g cat, 290g C_{30} oil

TARGET TEMP, C	280	265
PRESSURE, PSIG	153	500
FEED, NL/H g Fe	2.0	2.4



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PLT 700B RUN 25 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R16B234 72.7g cat, 290g C_{30} oil

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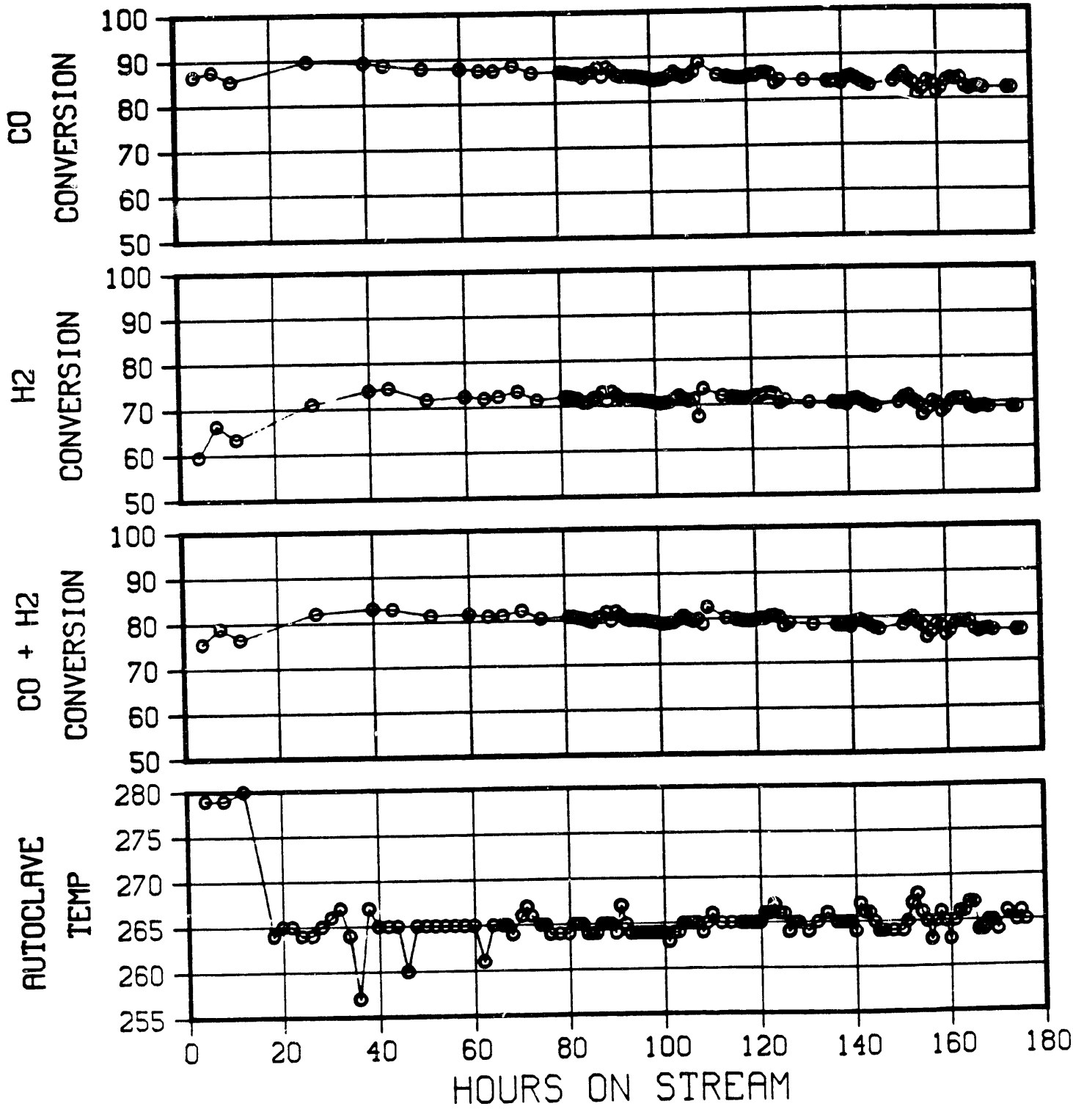
PRESSURE, PSIG	153	←	500 →
FEED, NL/H g Fe	2.0	←	2.4 →



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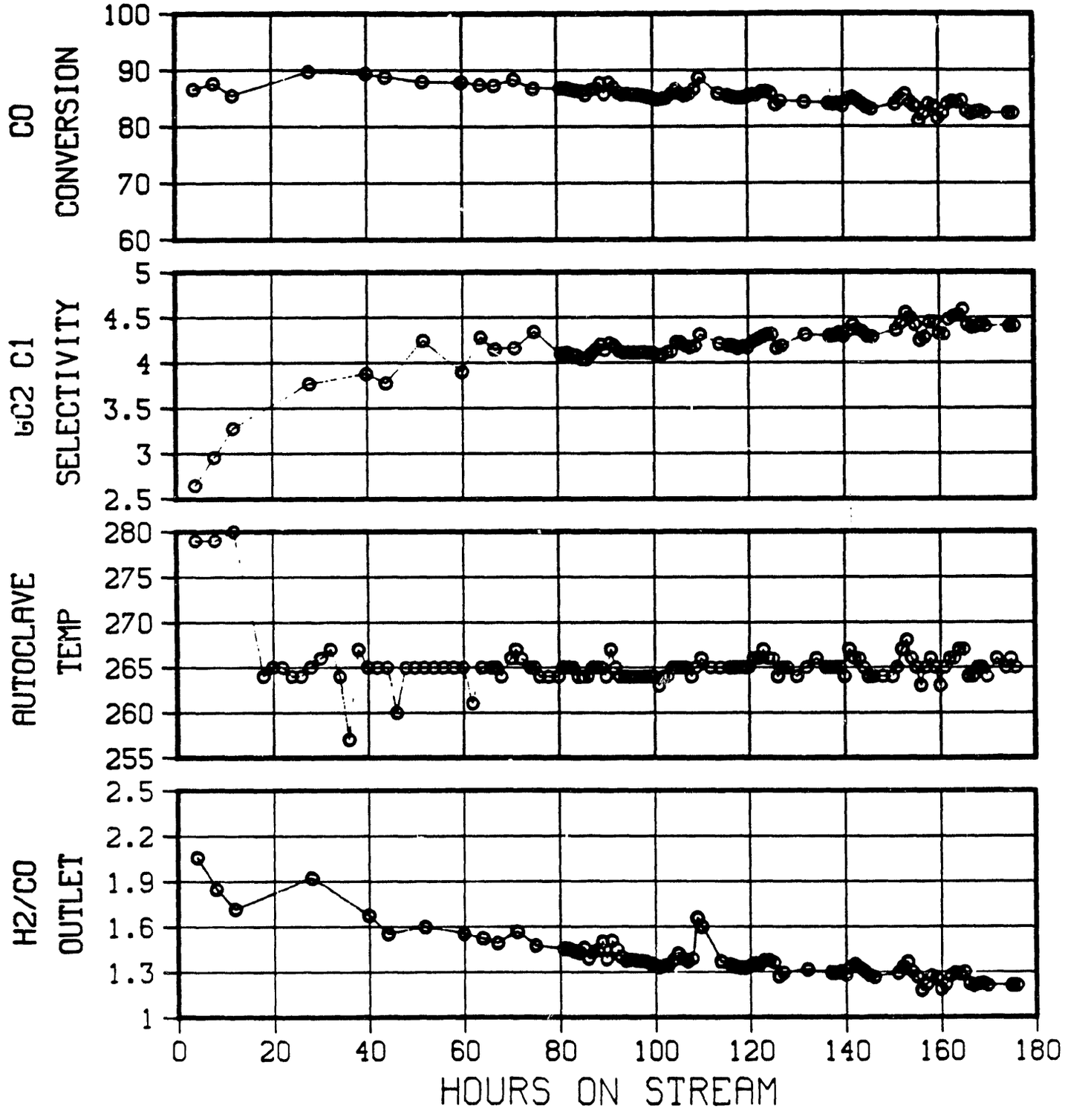

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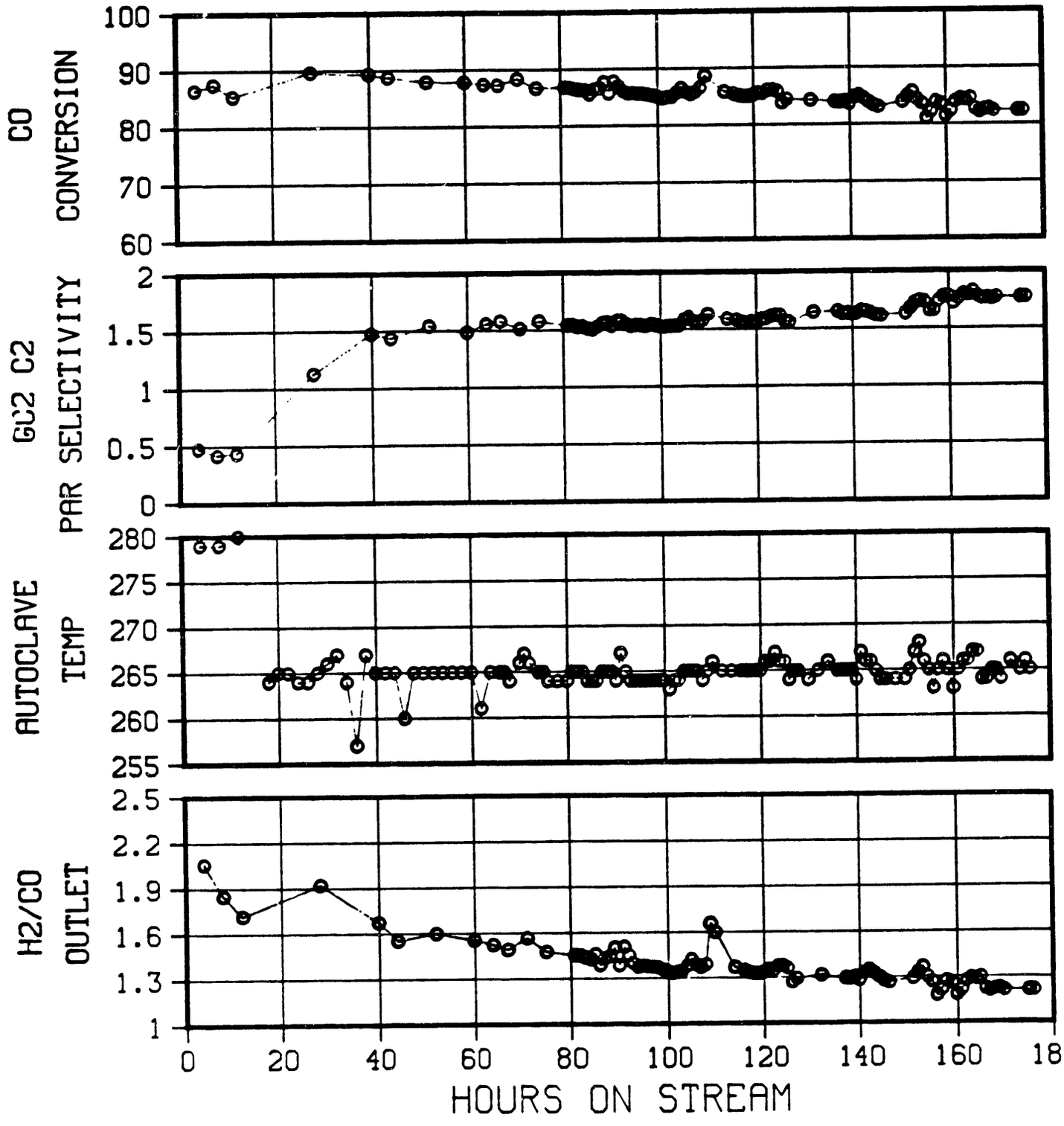

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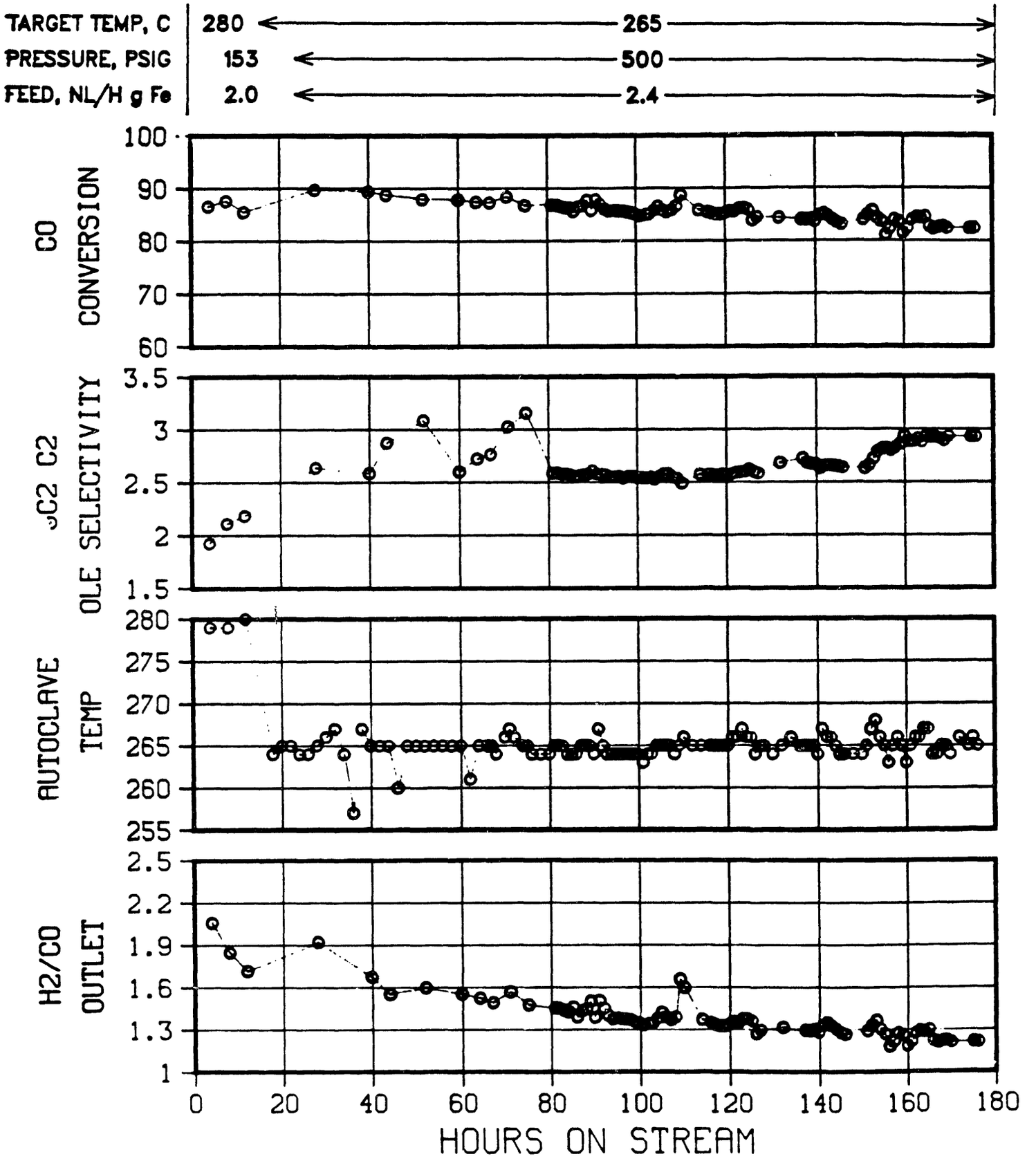
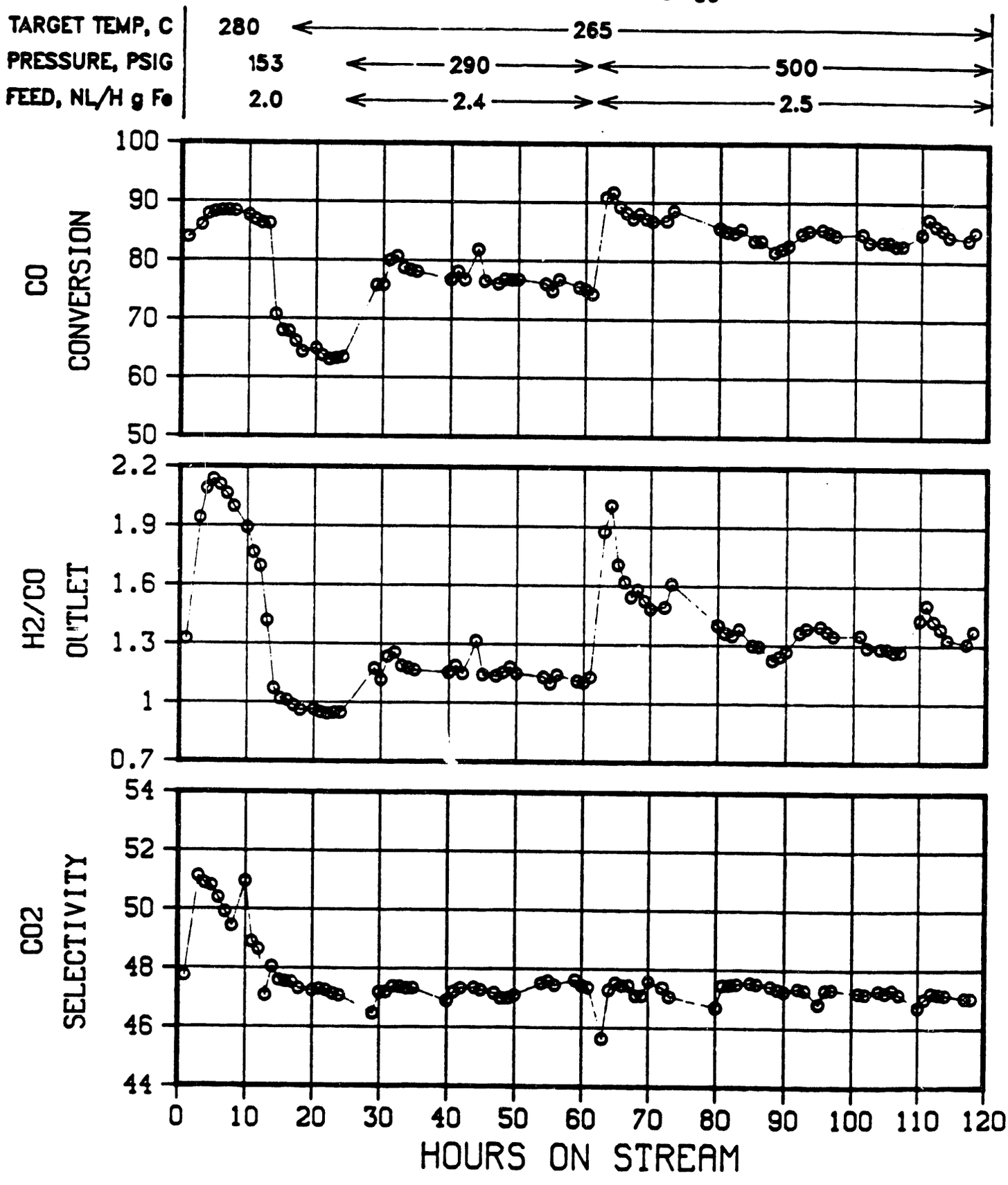


PRECIPITATED IRON CATALYST 6616-37 IN SLURRY AUTOCLAVE

PLT 700B RUN 26 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R16B234 72.7g cat, 290g C_{30} oil



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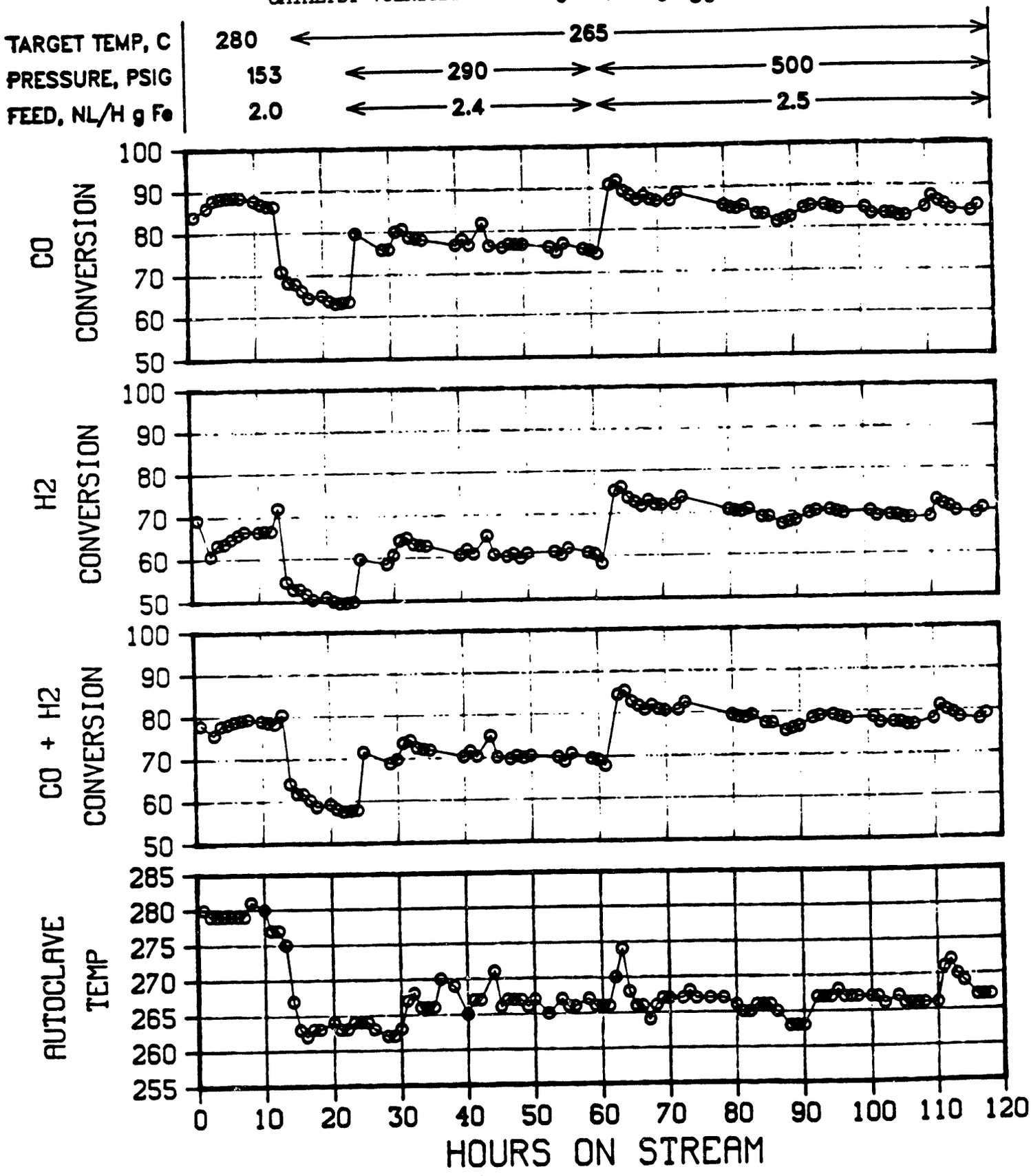

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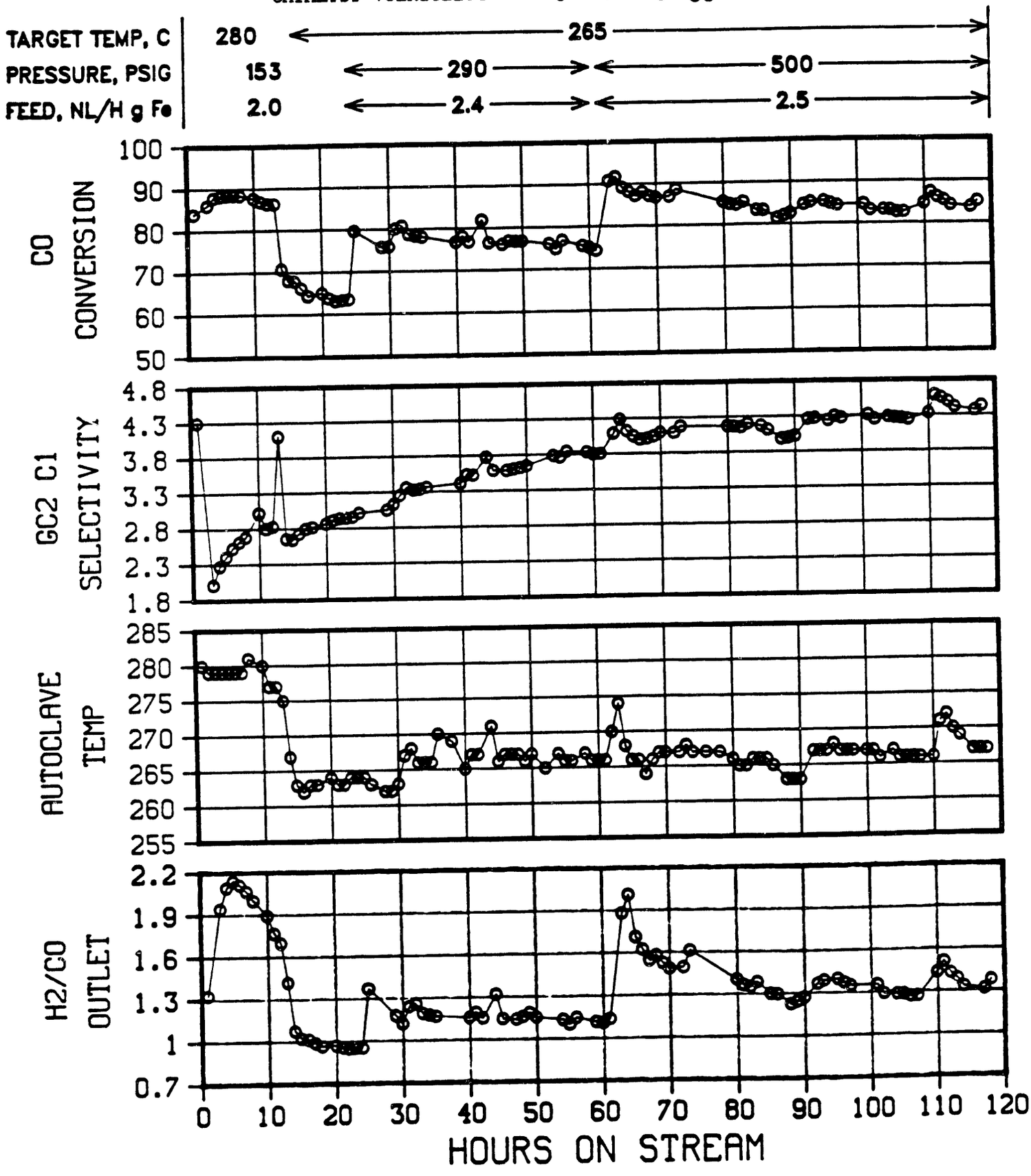

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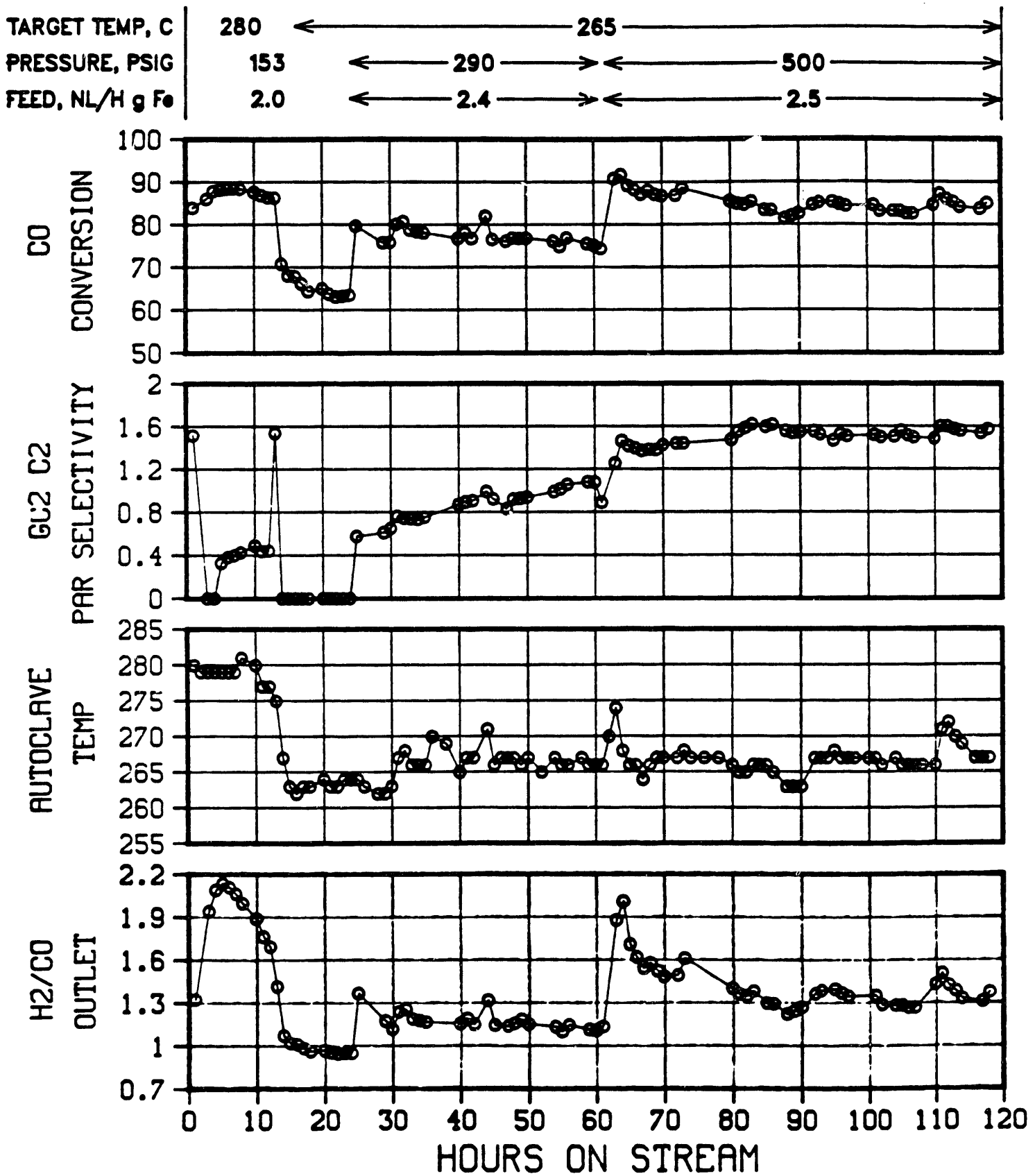

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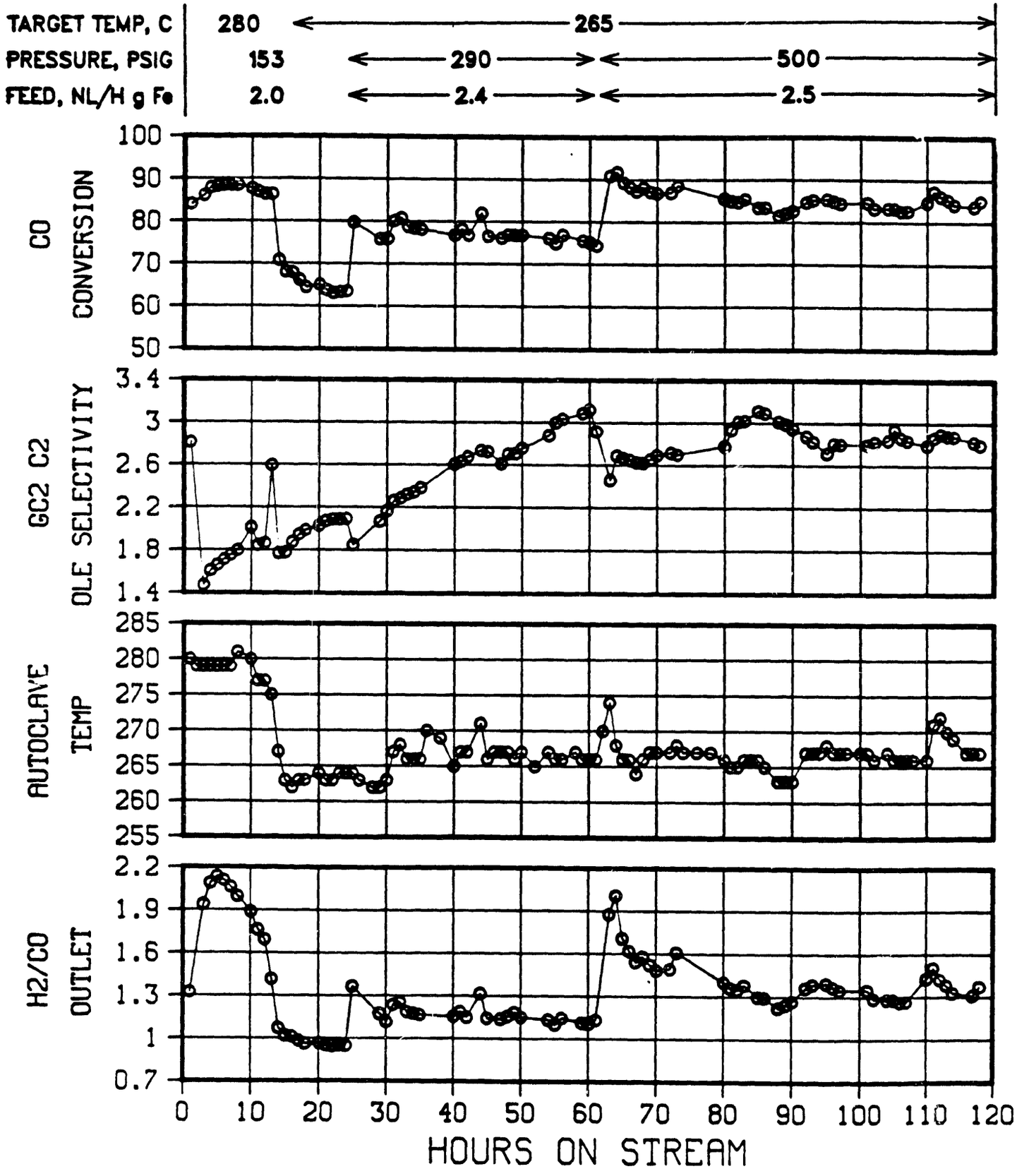
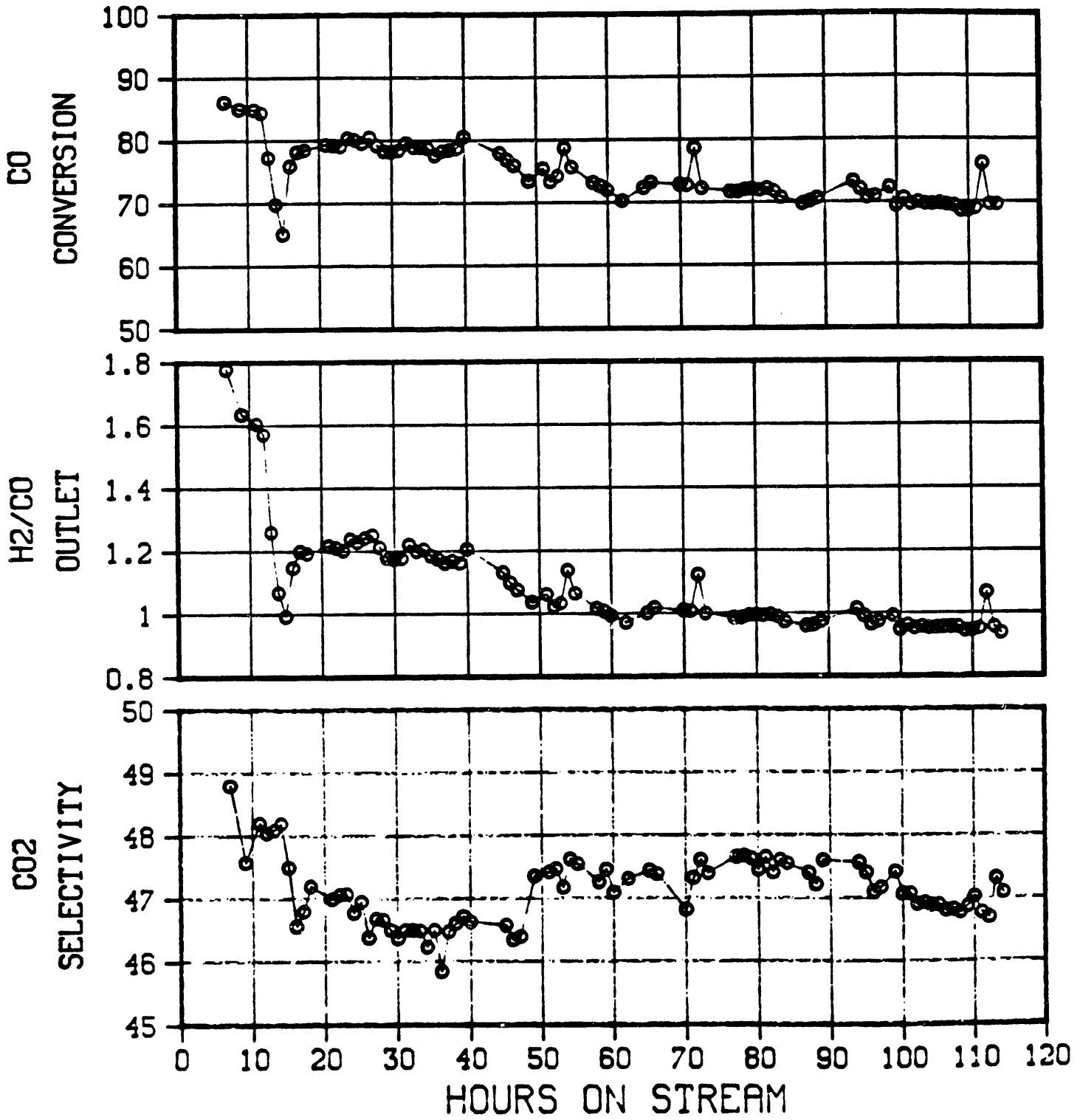


PRECIPITATED IRON CATALYST 6616–42 IN SLURRY AUTOCLAVE

PLT 700B RUN 27 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B200 72.7g cat, 290g C_{30} oil

TARGET TEMP, C	280	265
PRESSURE, PSIG	153	290
FEED, NL/H g Fe	2.0	2.4



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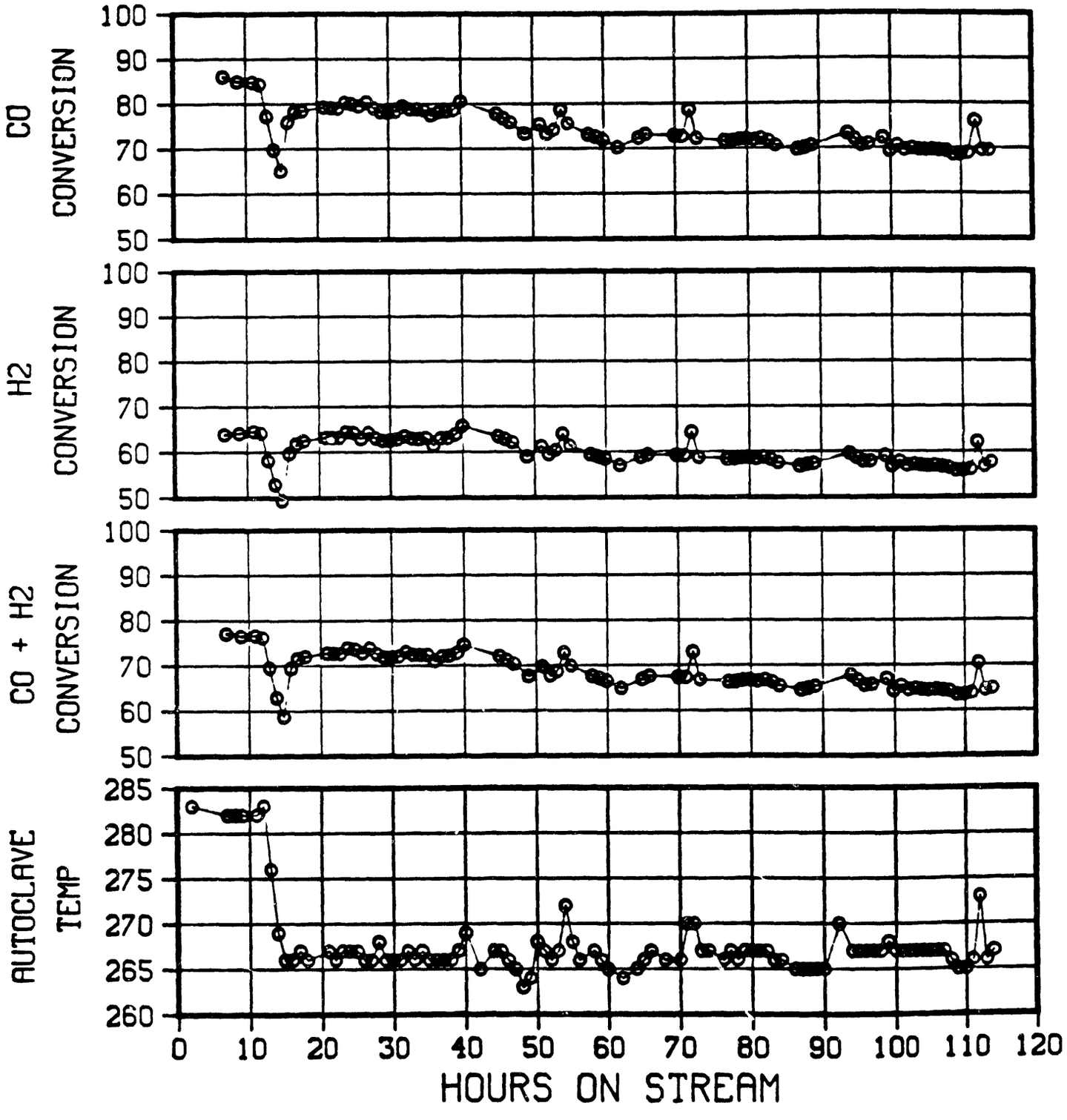

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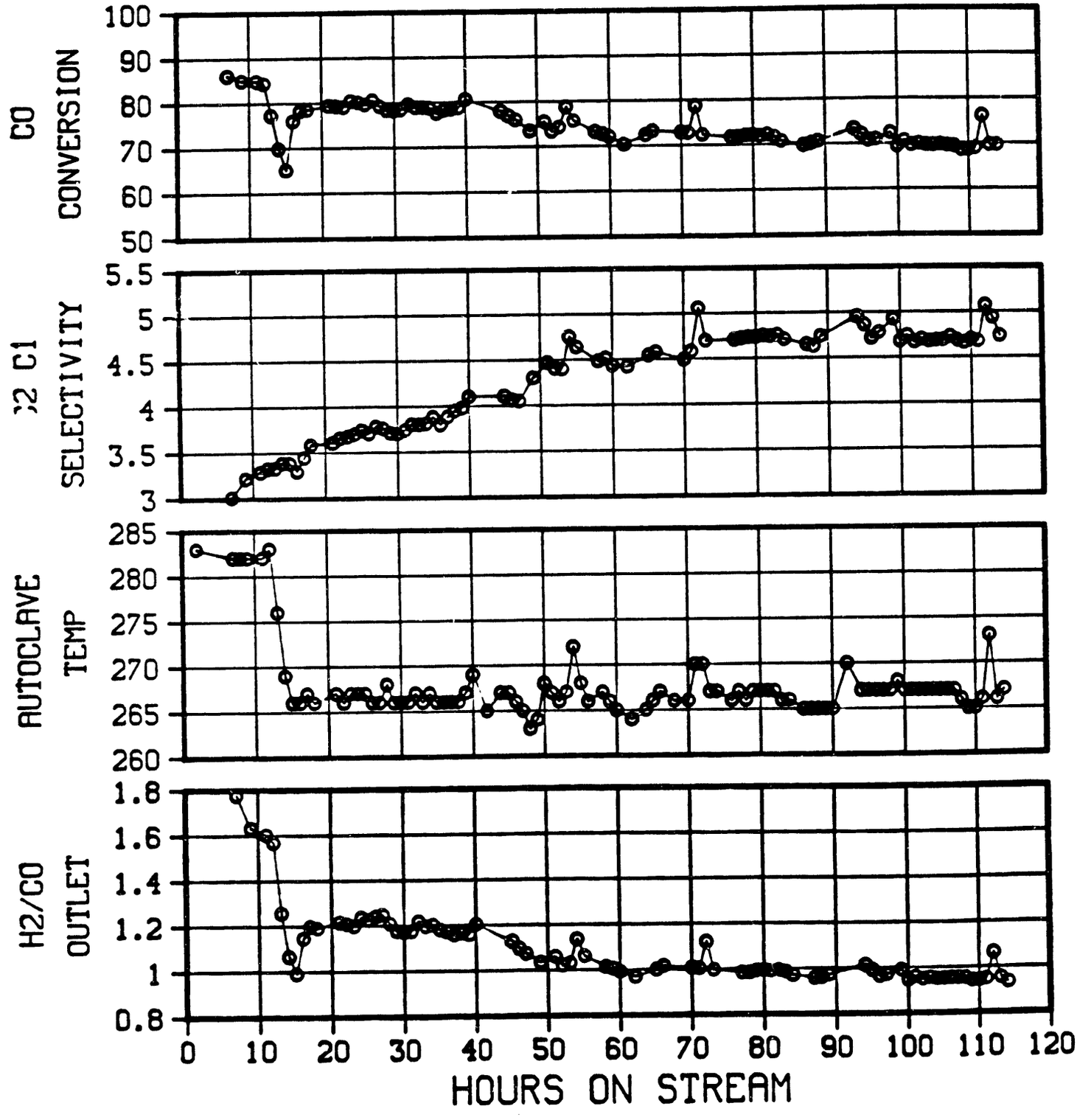

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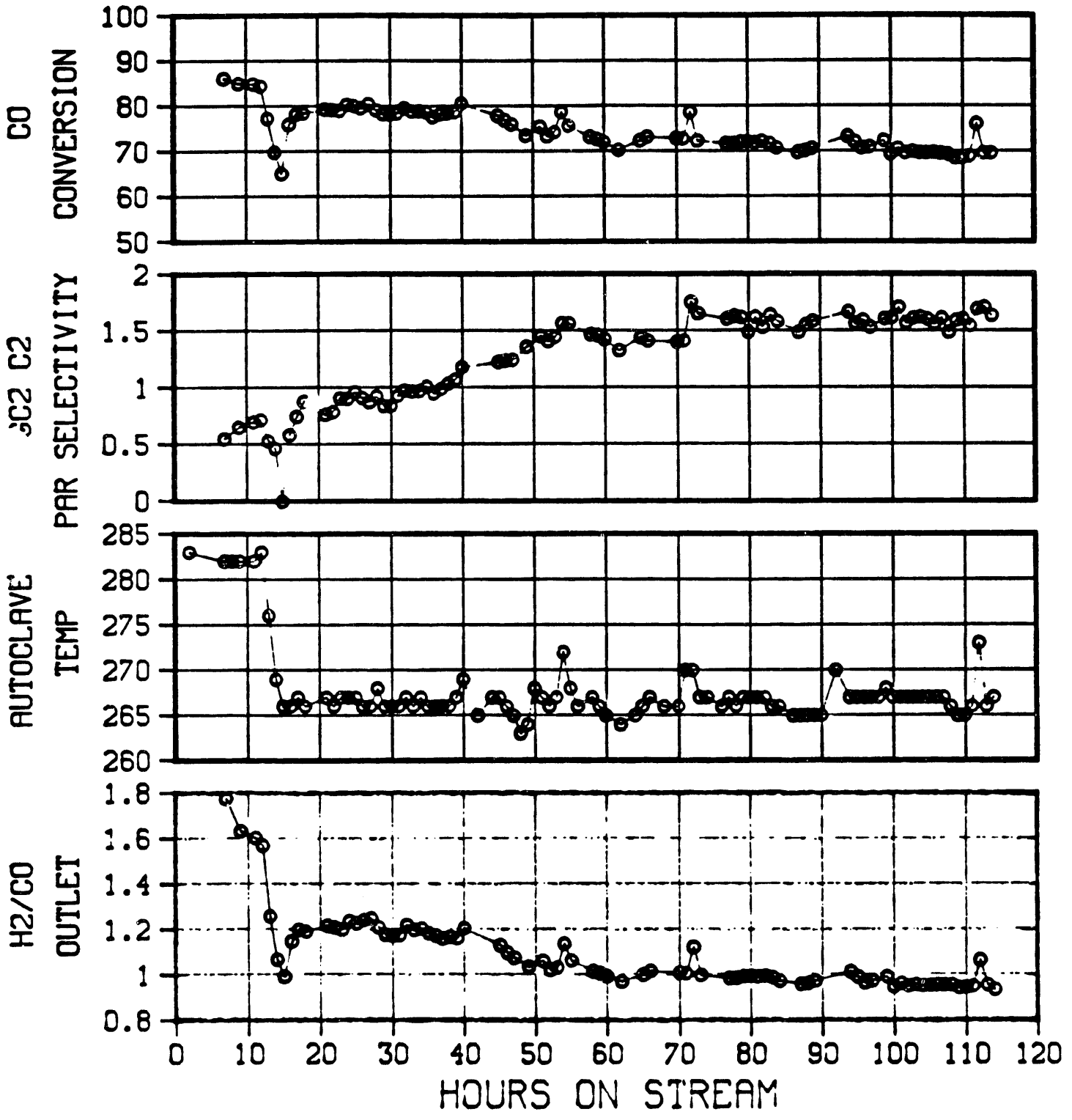

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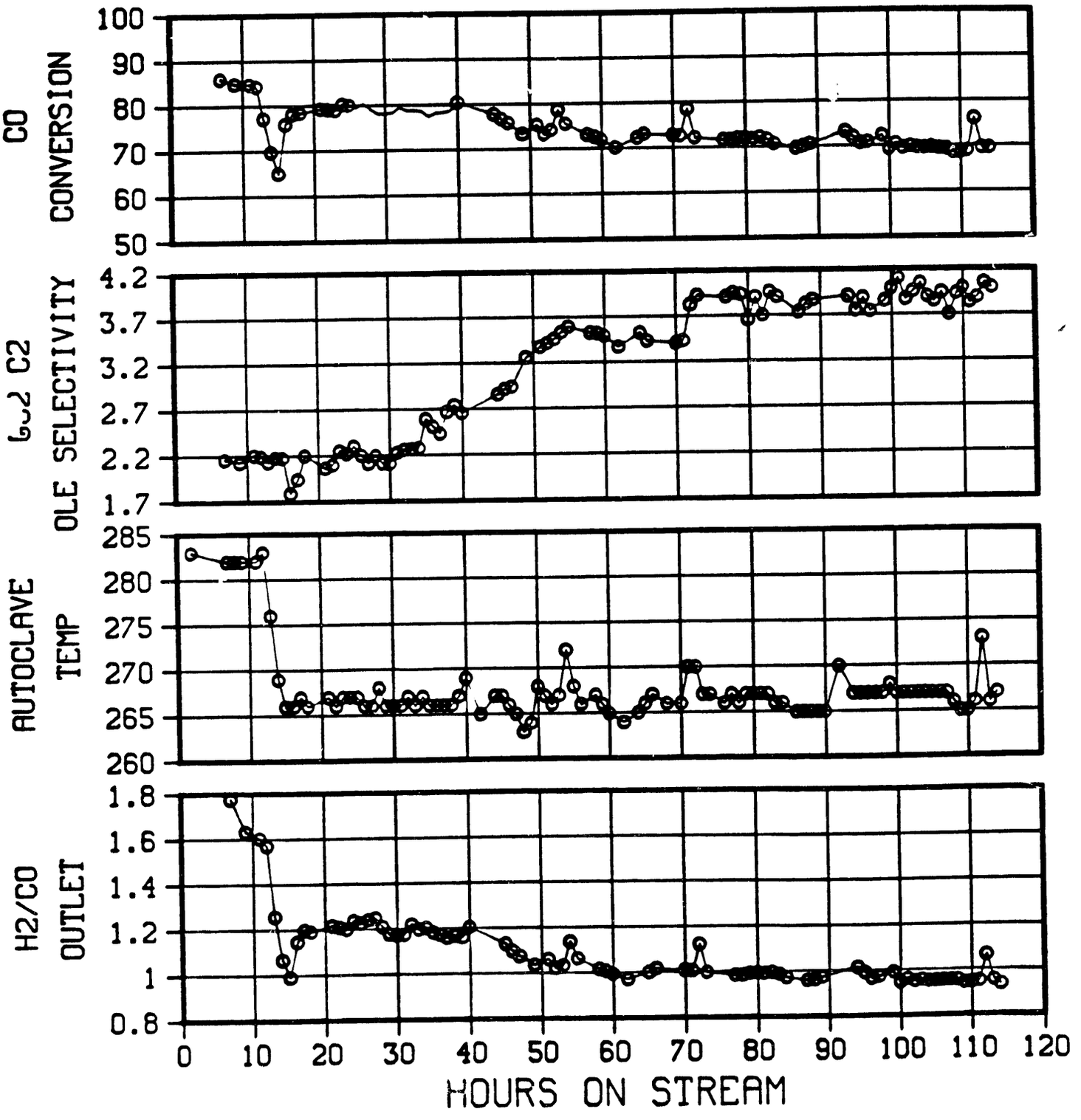

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