TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

Contract DE-AC22-90PC90055

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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 scale up procedure for large-scale synthesis of such catalysts for process development and long-term testing in slurry bubble-column reactors. 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. Typical feed used to attain this level of conversion is preferred to have H_2 and CO in the molar ratio of 0.5 to 1.0. 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

DISCLAIMER

SCOPE OF THE WORK DURING THE REPORTING PERIOD

A uniform lot of catalyst (752R17B7A) was prepared in sufficient quantity to allow five identical runs in the slurry autoclave plant. The first three runs (runs 28-30) allowed an assessment to be made of run-to-run reproducibility. The conversions at comparable times were almost identical in these runs. The reproducibility runs were of 100-hr duration. Initial catalyst activity was excellent. A fourth, 50-hr run (Run 32) was performed, during which catalyst samples were periodically withdrawn from the reactor for Mossbauer, magnetic susceptibility, and various wet chemical analyses. The results from these analyses are pending. A fifth, 375-hr run (Run 33) was performed to determine whether the excellent early conversions noted during the initial four runs persisted.

A reference catalyst from Ruhrchemie was also evaluated during this period. This catalyst gained activity throughout a 245-hr run, perhaps because it was not fully activated (reduced) by the standard activation procedures used in this work. Finally, an experimental catalyst (752R18B1A), which exhibited low activity, was evaluated in Run 34.

Task 2.0

Seven different runs (Run 28-34) were conducted in the slurry autoclave plant. The catalyst testing procedure and conversion-selectivity calculations were previously described in the technical progress report covering the period of 4/1/90-6/30/90 of the previous contract DE-AC22-87PC79812. Catalyst performance data from these runs are summarized in the appendix.

In all runs, 72.7 g of catalyst was loaded with 290 g of a C_{30} oil obtained from the Ethyl Corporation. The first part of each run was an activation procedure using the actual feed blend, which contained H_2 and CO in the molar ratio of 0.7. This procedure consisted of reducing the catalyst for 12 hr with the feed at a feed rate of 2 NL/hr/gFe and at temperature and pressure of 280°C and 153 psig, respectively. During the remainder of each run, the feed rate was 2.4 NL/hr/gFe, and the temperature was 265°C. The pressure during all of these runs was maintained at 290 psig.

Runs 28-30

These three runs were performed under identical conditions. Comparisons of conversion and selectivity are illustrated in the appendix. For the test period, run-to-run conversion differences were virtually nonexistent. Continual catalyst deactivation was noted. However, the runs were too

short to determine whether the activity would eventually line out. The conversions just after the catalyst activation period and at the end of the runs were high compared with those from previous catalysts prepared in this laboratory. Methane, ethane, and ethylene selectivities were close at most times during these runs although some variation was noted at the end of the runs. For instance, run-to-run methane and ethane selectivities varied from 3.9 to 4.5% and 1.2 to 1.4% respectively at 100 hr. Carbon dioxide selectivity was high throughout the runs as expected for the iron catalysts. At any time during the tests, the run-to-run variation in this selectivity was no more than one percent.

Run 31

A sample of a Ruhrchemie reference catalyst was evaluated. This catalyst was analyzed here as follows:

Elemental Analysis (g/100gFe):

Cu	5.07
K	3.08
Si	10.96

Surface Area (m^2/g): 312.6

In the standard test, CO conversion was 66% after the catalyst activation period. This conversion is lower than the CO conversion attained with catalysts prepared here during the current study. However, for the Ruhrchemie catalyst, the CO conversion increased continuously as the run progressed. The usual activation procedure might not have been extensive enough to fully reduce (activate) the catalyst. By the end of the 245-hr run, the CO conversion appeared to be lining out at about 71%, which is in the conversion range observed with the catalysts prepared in this laboratory. The sum of methane and ethane selectivities seemed to be lining out at about 7.7%. This catalyst appears to produce greater quantities of light ends than are desired for the current work.

Run 32

This run was carried out for only 50 hr. It used a fresh sample of catalyst 752R17B7A, which was used in Runs 28-30. Catalyst and wax samples were withdrawn from the reactor at 1, 4, 12, 24, and 47 hr. These samples, a sample from the reactor at the end of the run, and a sample of unused catalyst were submitted for Mossbauer and magnetic measurements as well as various wet chemical analyses. These tests have not yet been completed.

Run 33

This run was carried put for a period of 375 hr. It also used a fresh sample of catalyst 752R17B7A, which was used in Runs 28-30. The purpose of this run was to determine whether the high conversions noted in the 100-hr runs (Runs 28-30) persisted. The maximum conversion was slightly less than the maximum conversion attained during Runs 28-30. Also, a slightly faster rate of catalyst deactivation was apparent after the catalyst activation procedure; a deactivating agent not present during Runs 28-30 could have been responsible. In the pilot plant set up, molecular sieves are used to remove feed impurities. The molecular sieves may have lost the ability to remove impurities between Runs 30 and 33. In the future, they will be changed more often to eliminate this problem. By 175 hr, the catalyst activity had lined out; the CO conversion was 75%, and was maintained at that level until the end of the run 200 hr later. This lined-out conversion is in the high range for iron catalysts evaluated in this work, but it does not meet the target set for this project. The methane and ethane selectivities were 4.6% and 1.4% respectively at the end of the run.

Run 34

An experimental catalyst (752R18B1A), which exhibited low activity, was evaluated. The CO conversion was only 11% after the catalyst activation period. The methane selectivity was 7%.

Because of the observed low activity, the run was terminated at 55 hr. This catalyst contained a third component not present in other catalysts prepared so far in this laboratory. In the future, additional catalysts with lower levels of this component will be prepared and tested.

CONCLUSIONS

The slurry autoclave test is very reproducible, as was demonstrated by performing three runs under identical conditions. Each run used a fresh sample of catalyst (752R17B7A) from the same preparation. For instance, at any time on-stream, the run-to-run variation in CO conversion was at most 2% for conversions in the range of 82 to 91%. Selectivities to light products were also evaluated and found to be close for a major part of the runs.

Two additional runs were performed under the same conditions as the three reproducibility runs. One of these runs was a short run (Run 32), and during which, samples of wax and catalyst were withdrawn for Mossbauer and magnetic measurements. The other run (Run 33) was the longest of the five and demonstrated that the high catalyst activities during the 100-hr reproducibility runs did not persist. Although the line-out activity was high, it was not higher than that observed with some active catalysts prepared previously in this laboratory.

A commercially available Fischer-Tropsch catalyst from Ruhrchemie was also evaluated during this quarter. By the end of a 240-hr run, this catalyst seemed to be lining out at about 71% to 72% CO conversion. At this time, the sum of methane and ethane selectivities was 7.7%.

Finally, catalyst 752R18B1A, which exhibited low activity, was evaluated. The catalyst was prepared by adding a third component to the iron-copper oxide prior to its impregnation. In the future, catalysts with lower levels of this third component will be prepared and tested.

APPENDIX

SUMMARY OF RUNS 28-34, PLANT 700B

COMPARISON OF RUNS 28,29 & 30, CATALYST 6616-49

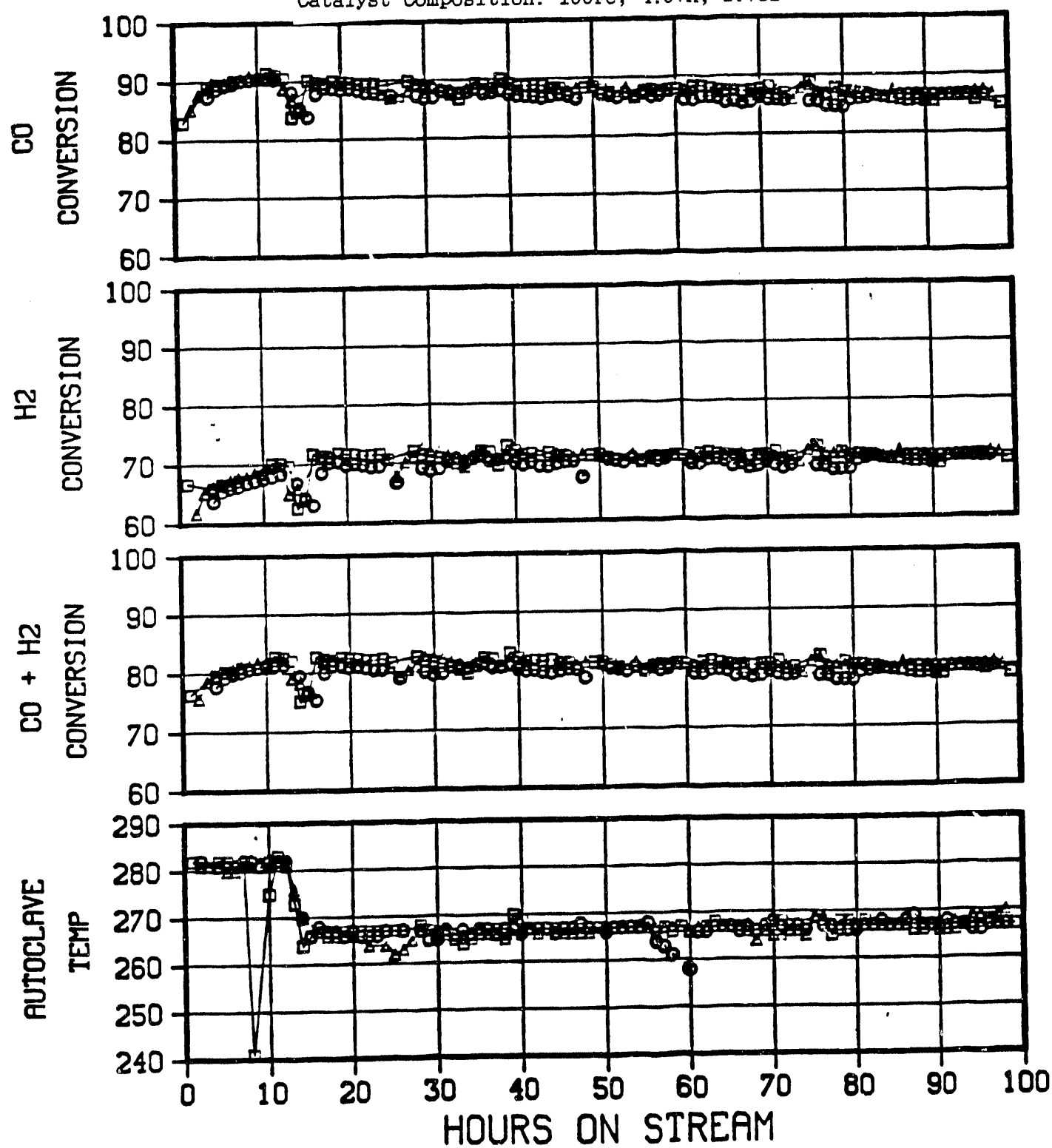
H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 △
RUN 29 □
RUN 30 ○

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

Catalyst Composition: 100Fe, 4.07X, 1.78Z



COMPARISON OF RUNS 28,29 & 30, CATALYST 6616-49

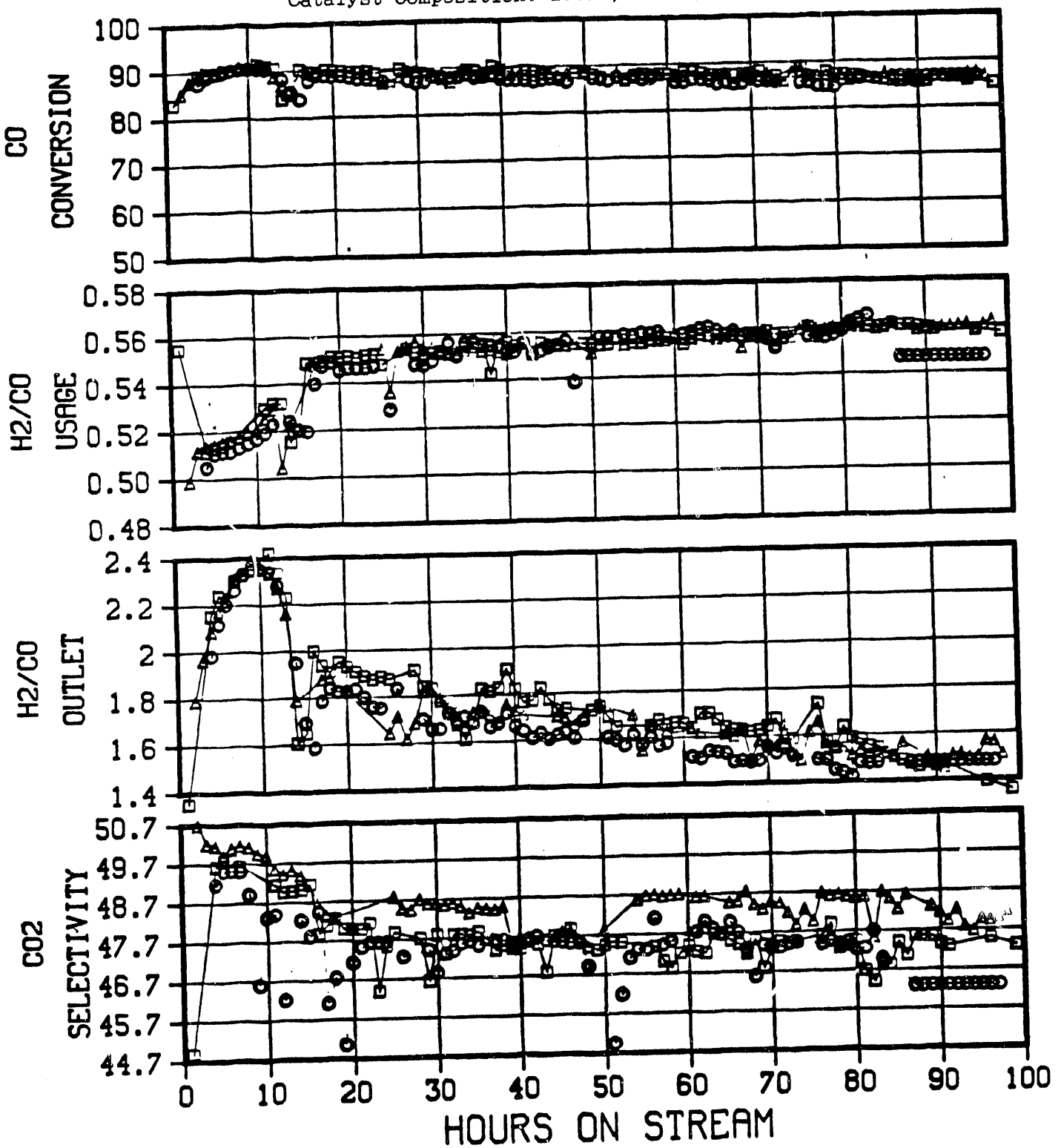
H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 △
RUN 29 □
RUN 30 ○

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

Catalyst Composition: 100Fe, 4.07X, 1.78Z



COMPARISON OF RUNS 28,29 & 30, CATALYST 6616-49

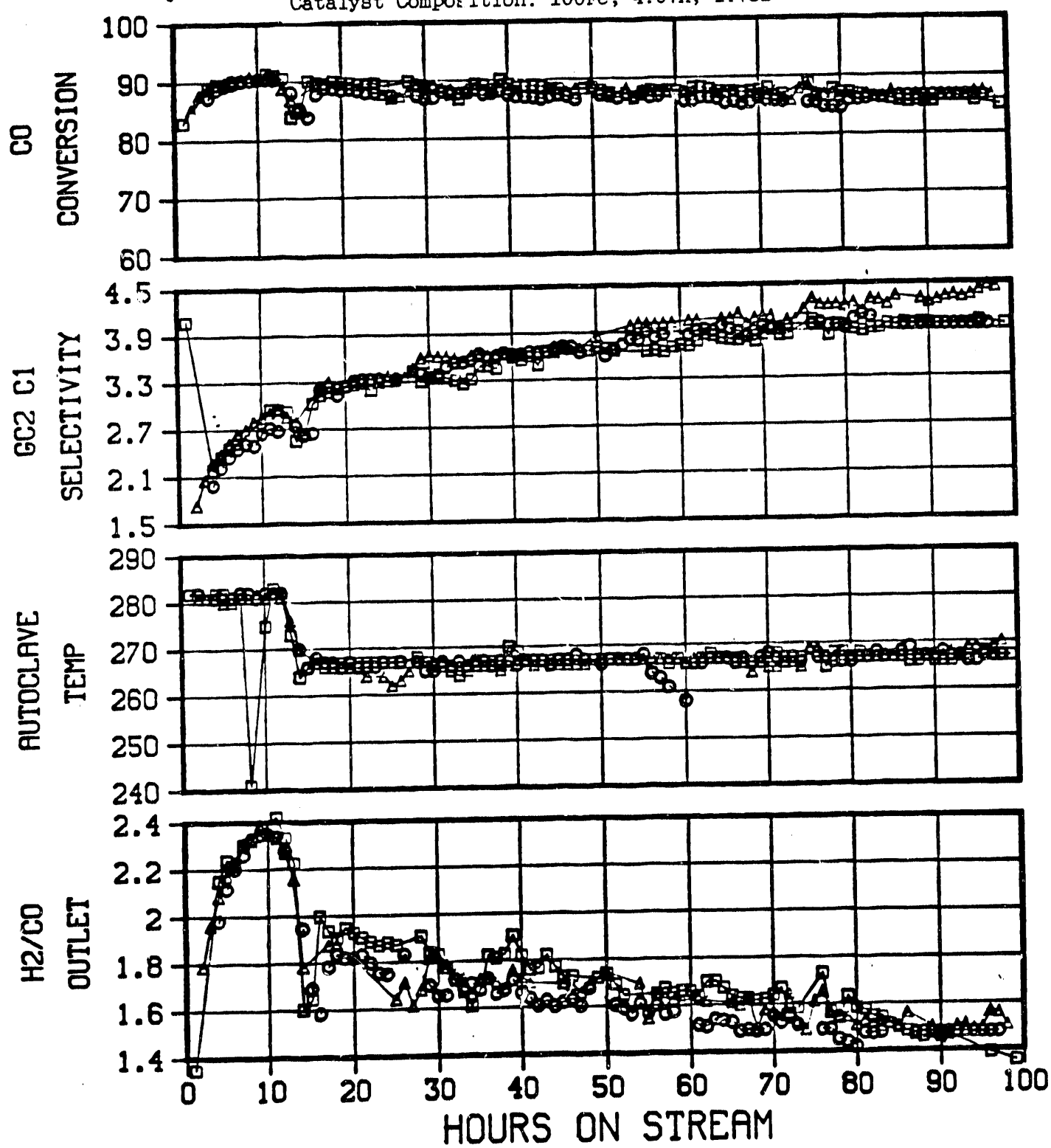
H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 △
RUN 29 □
RUN 30 ○

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

Catalyst Composition: 100Fe, 4.07X, 1.78Z



COMPARISON OF RUNS 28,29 & 30, CATALYST 6616-49

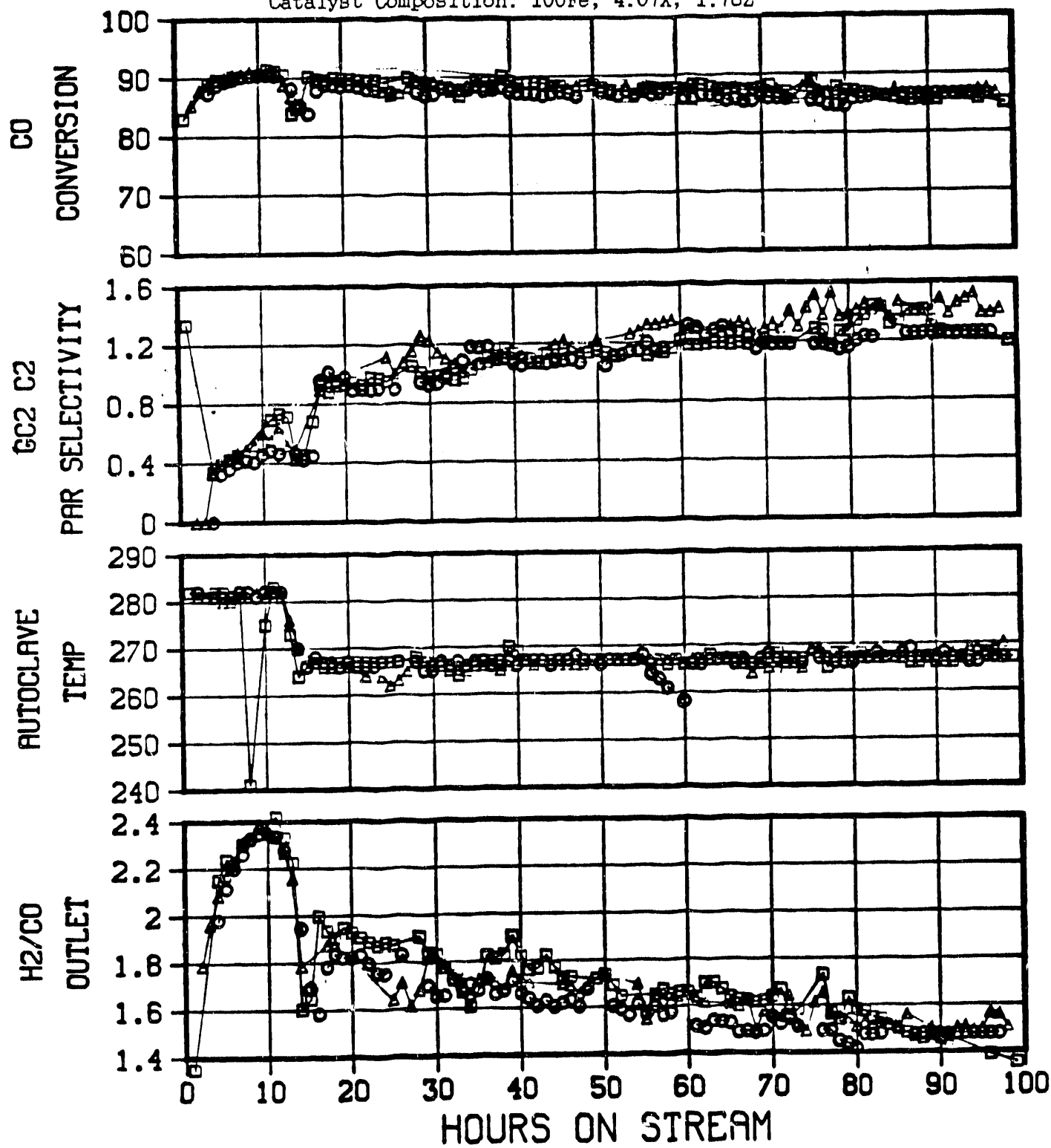
H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 △
RUN 29 □
RUN 30 ○

TARGET TEMP, C	280	285	
PRESSURE, PSIG	153	290	
FEED, NL/H g Fe	2.0	2.4	

Catalyst Composition: 100Fe, 4.07X, 1.78Z



COMPARISON OF RUNS 28,29 & 30, CATALYST 6616-49

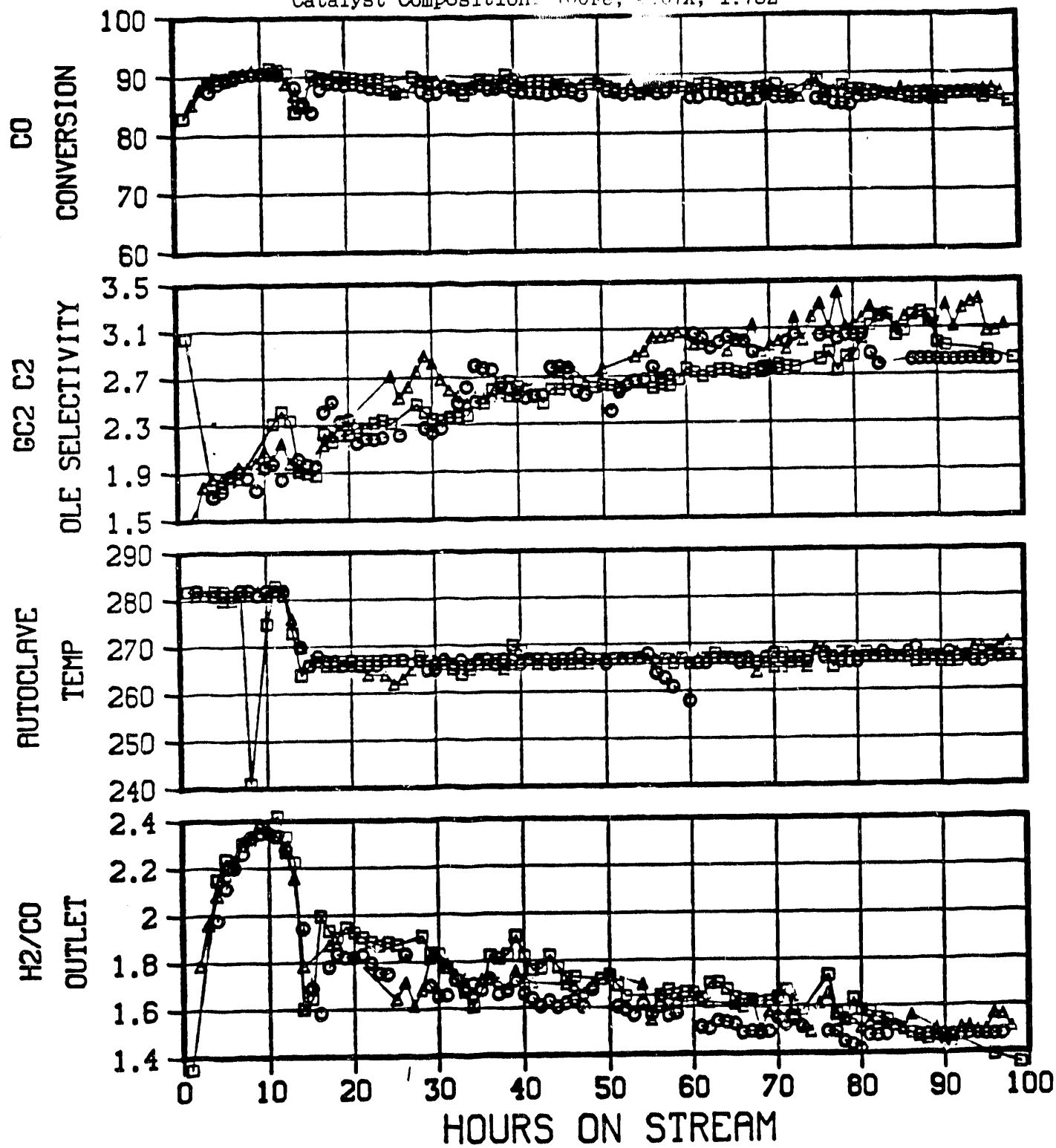
H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

RUN 28 △
RUN 29 □
RUN 30 ○

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

Catalyst Composition: 100Fe, 4.07X, 1.78Z

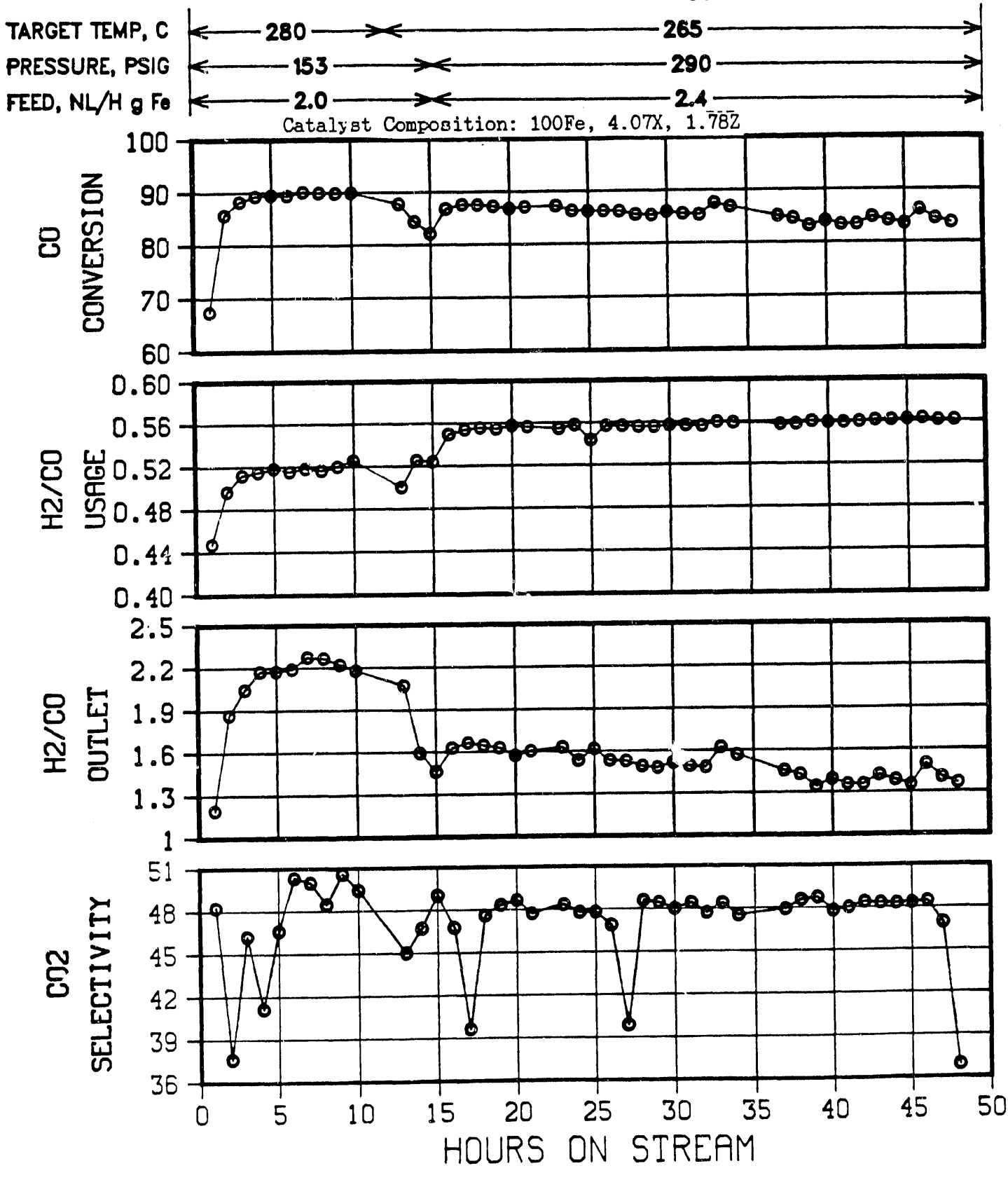


PRECIPITATED IRON CATALYST 6616-49 IN SLURRY AUTOCLAVE

CATALYST WITHDRAWAL EXPERIMENT

PLT 700B RUN 32 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

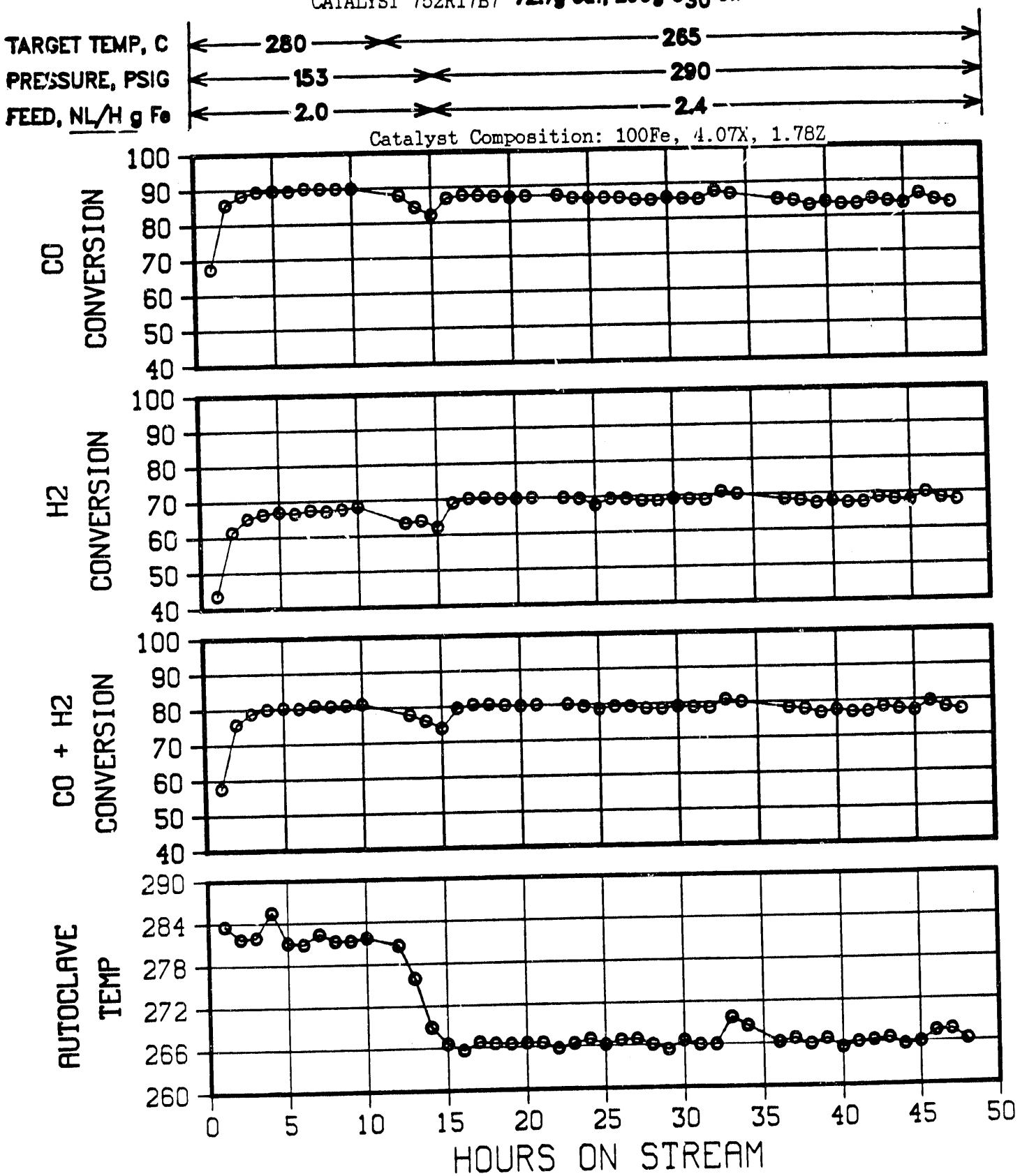


PRECIPITATED IRON CATALYST 6616-49 IN SLURRY AUTOCLAVE

CATALYST WITHDRAWAL EXPERIMENT

PLT 700B RUN 32 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

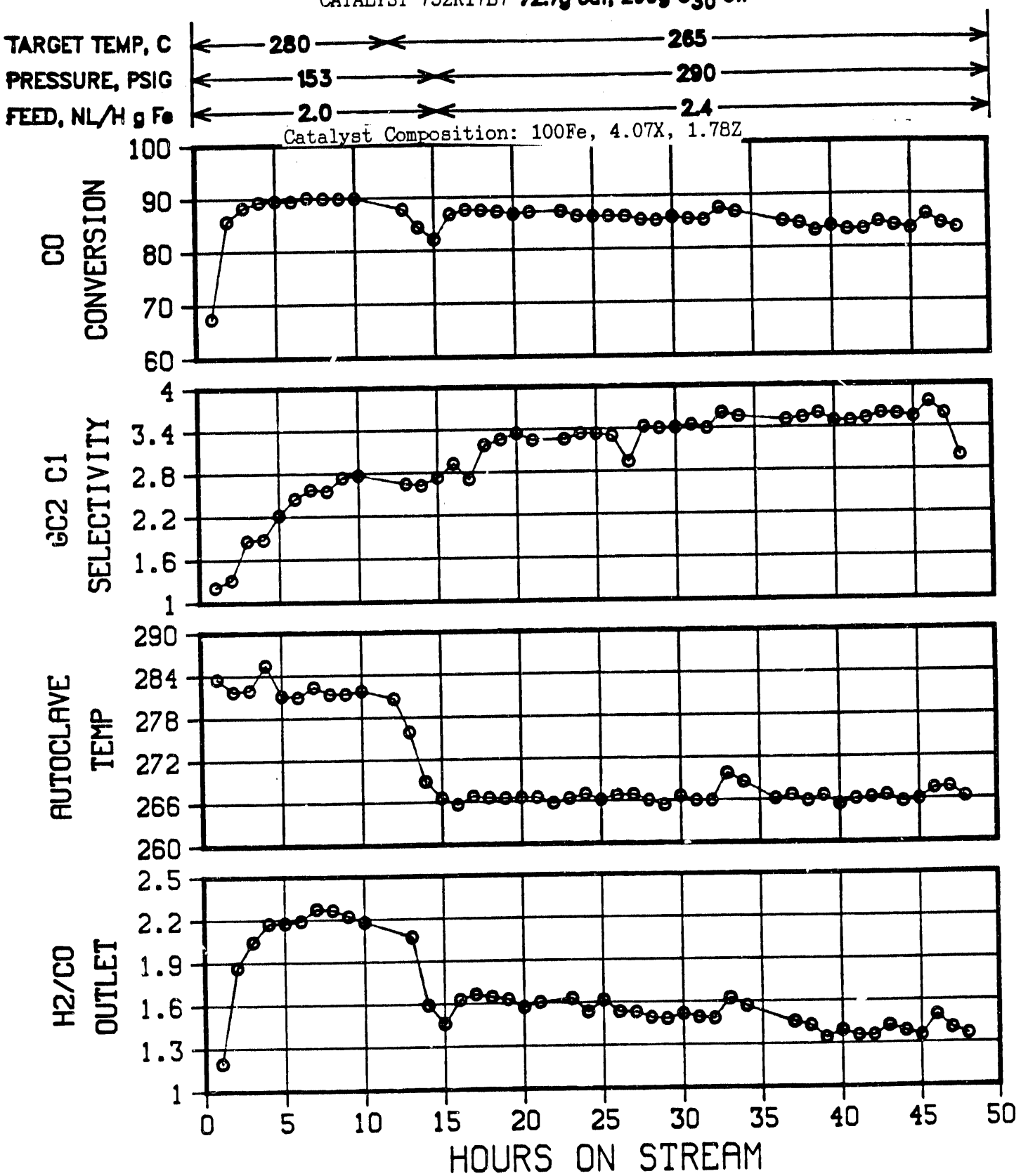


PRECIPITATED IRON CATALYST 6616-49 IN SLURRY AUTOCLAVE

CATALYST WITHDRAWAL EXPERIMENT

PLT 700B RUN 32 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

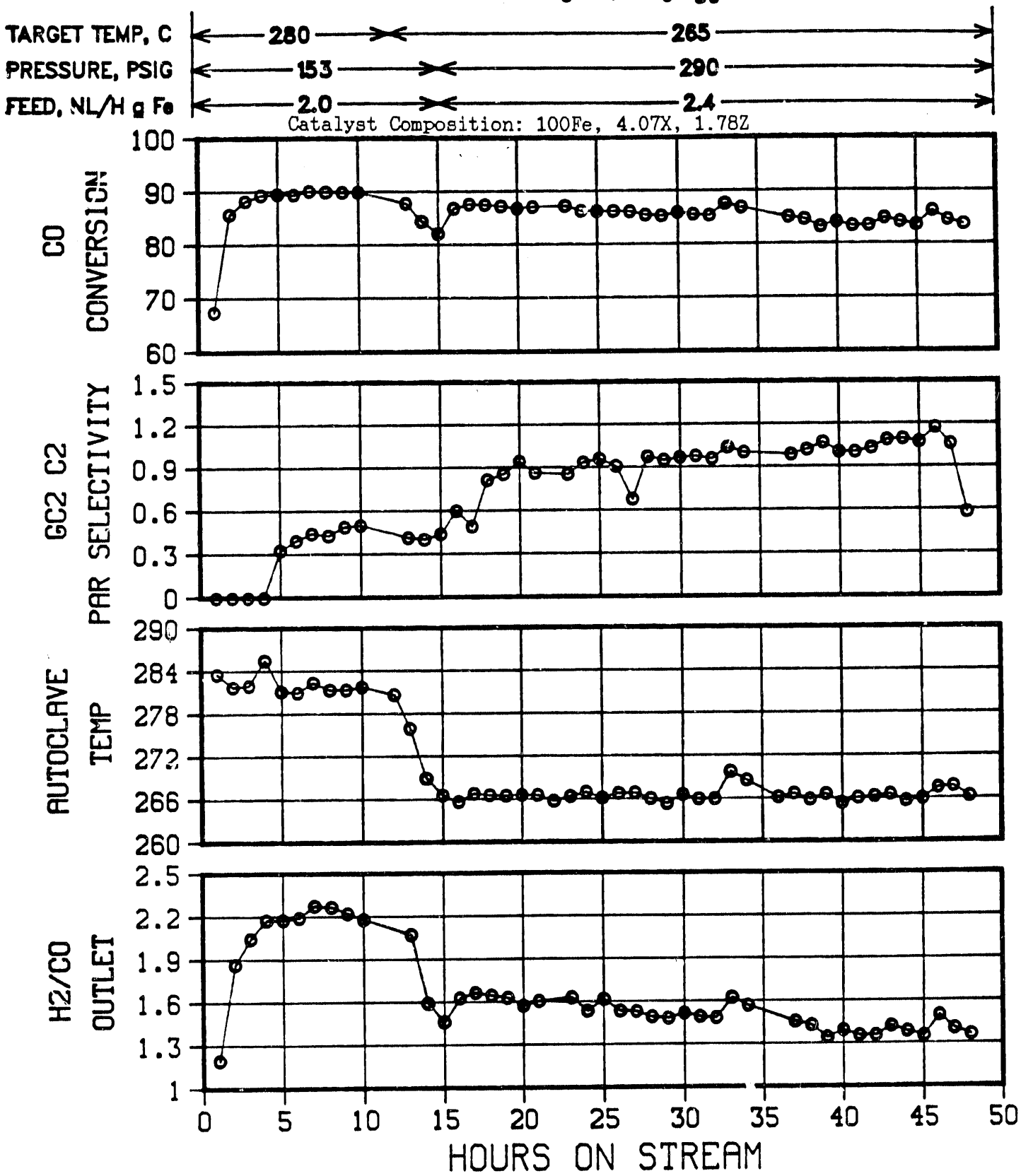


PRECIPITATED IRON CATALYST 6616-49 IN SLURRY AUTOCLAVE

CATALYST WITHDRAWAL EXPERIMENT

PLT 700B RUN 32 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil

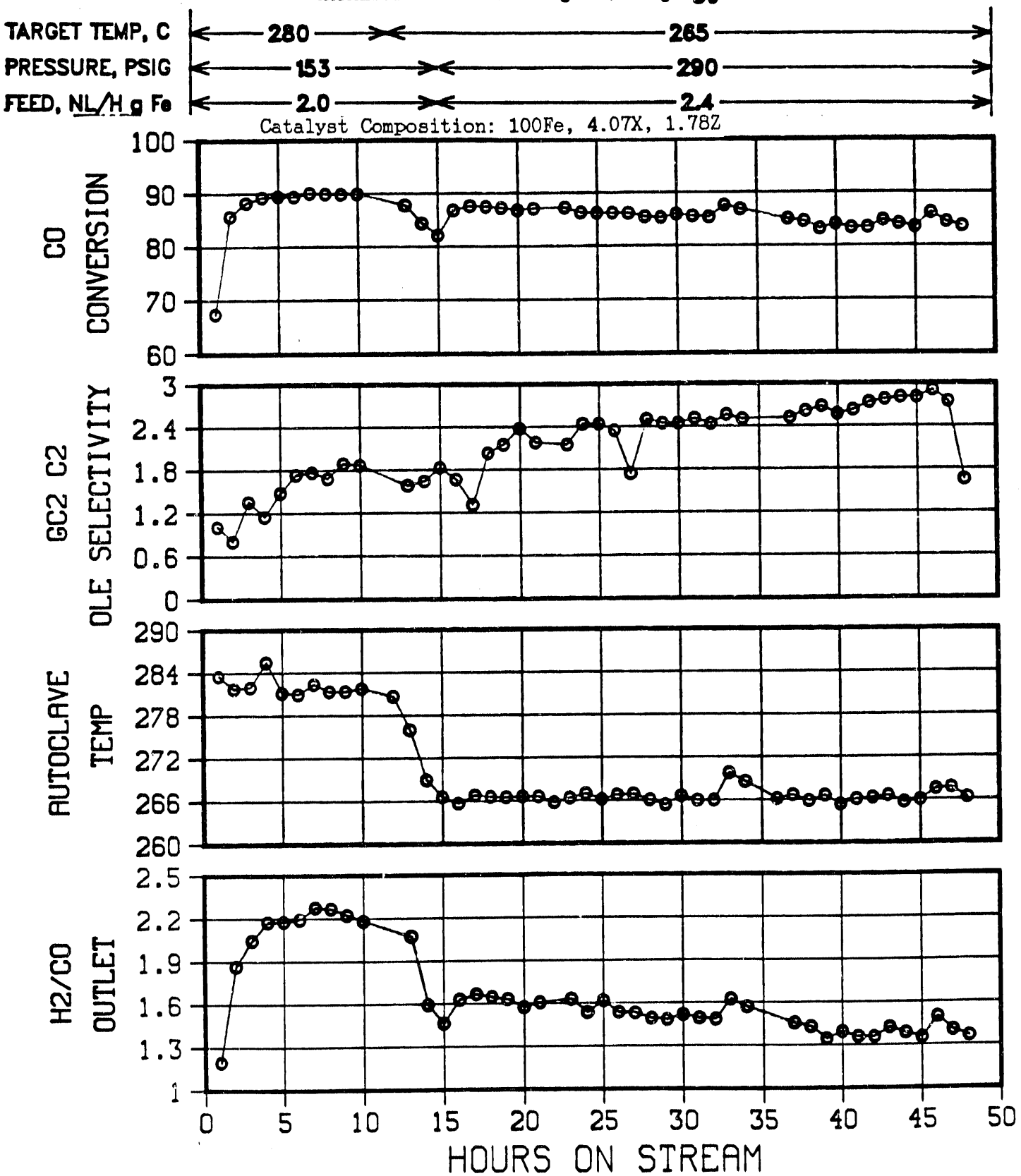


PRECIPITATED IRON CATALYST 6616-49 IN SLURRY AUTOCLAVE

CATALYST WITHDRAWAL EXPERIMENT

PLT 700B RUN 32 H_2:CO feed = 0.7, 1100 rpm

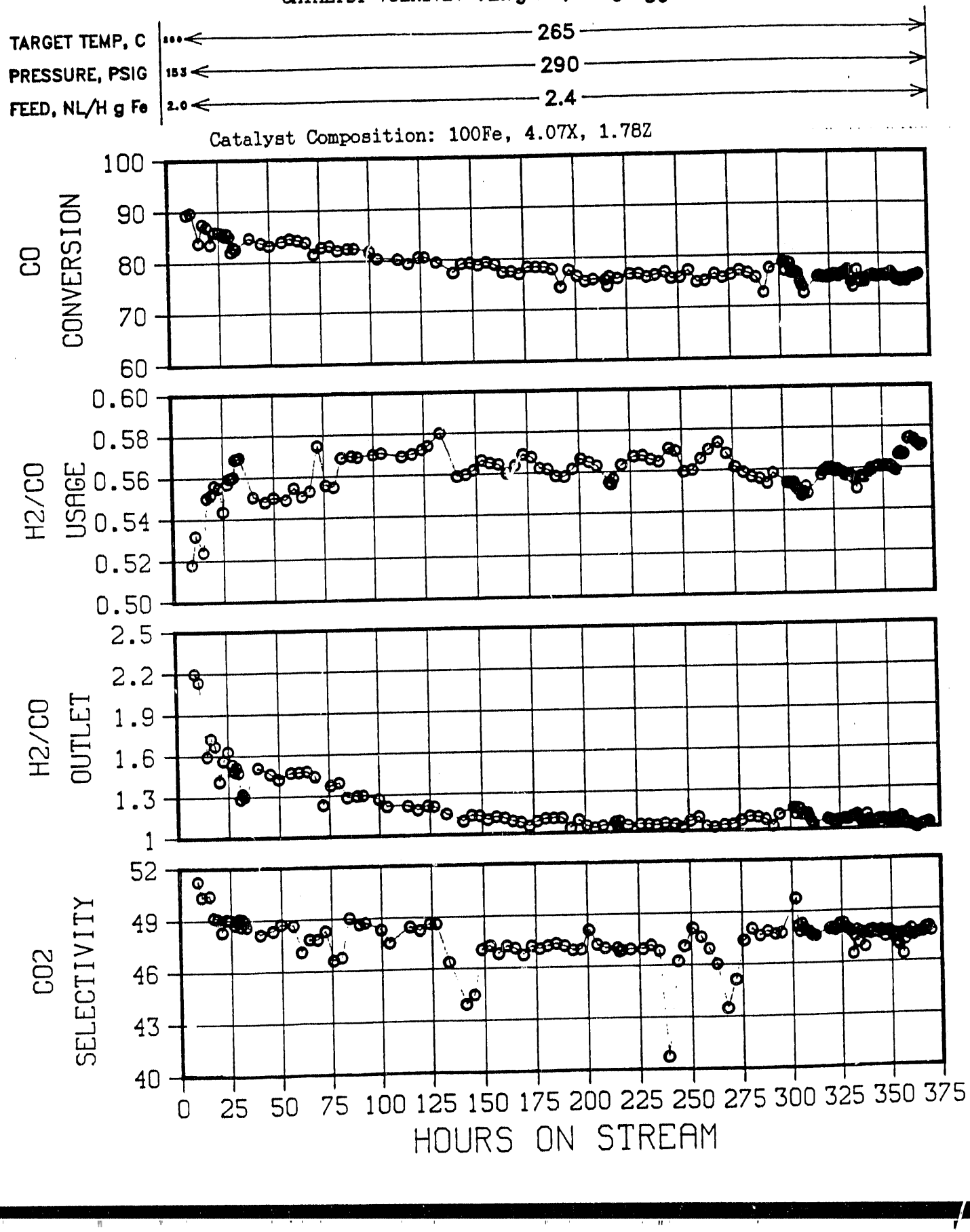
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil



PRECIPITATED IRON CATALYST 6616–49 IN SLURRY AUTOCLAVE

PLT 700B RUN 33 H_2:CO feed = 0.7, 1100 rpm

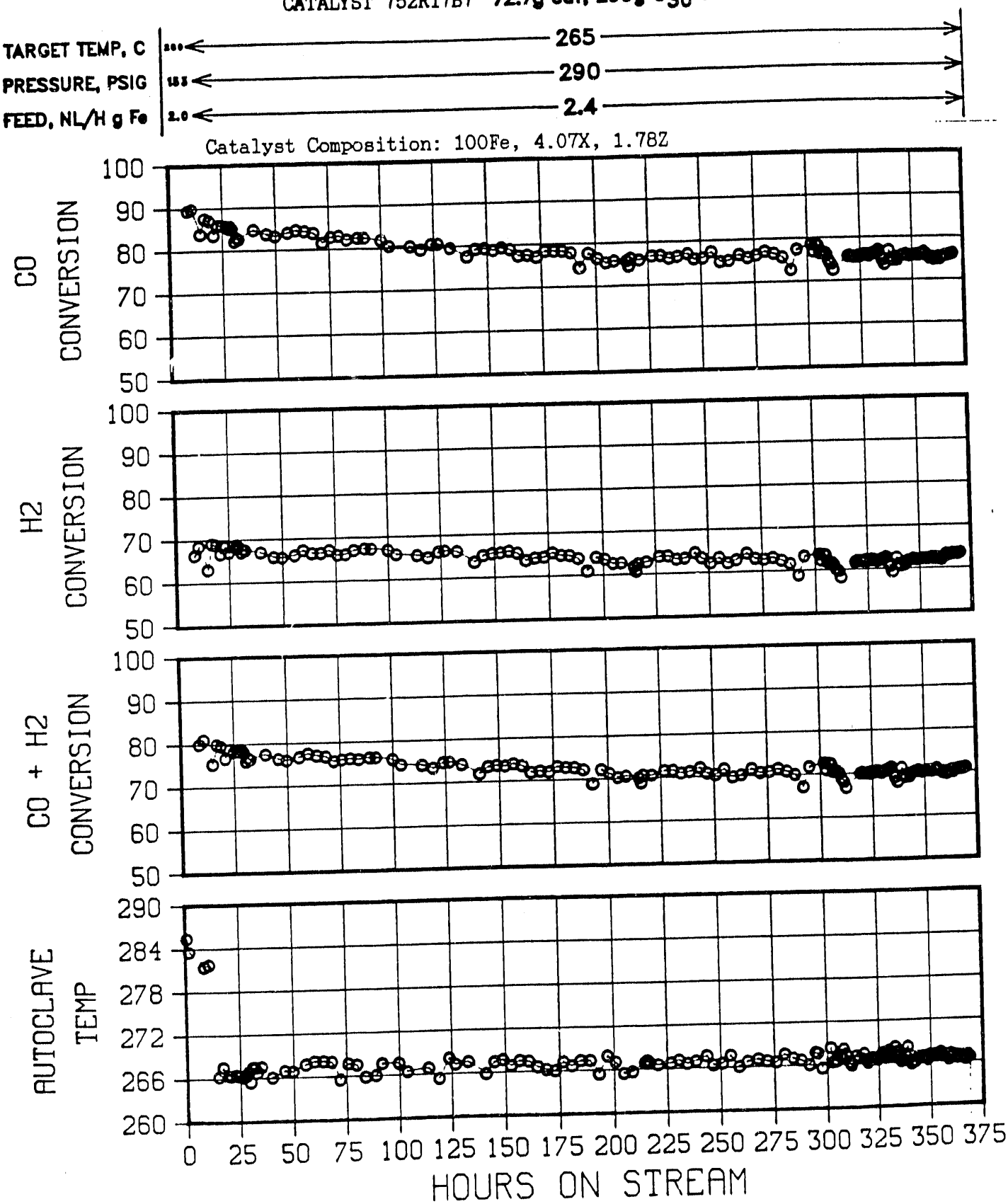
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil



PRECIPITATED IRON CATALYST 6616–49 IN SLURRY AUTOCLAVE

PLT 700B RUN 33 H_2:CO feed = 0.7, 1100 rpm

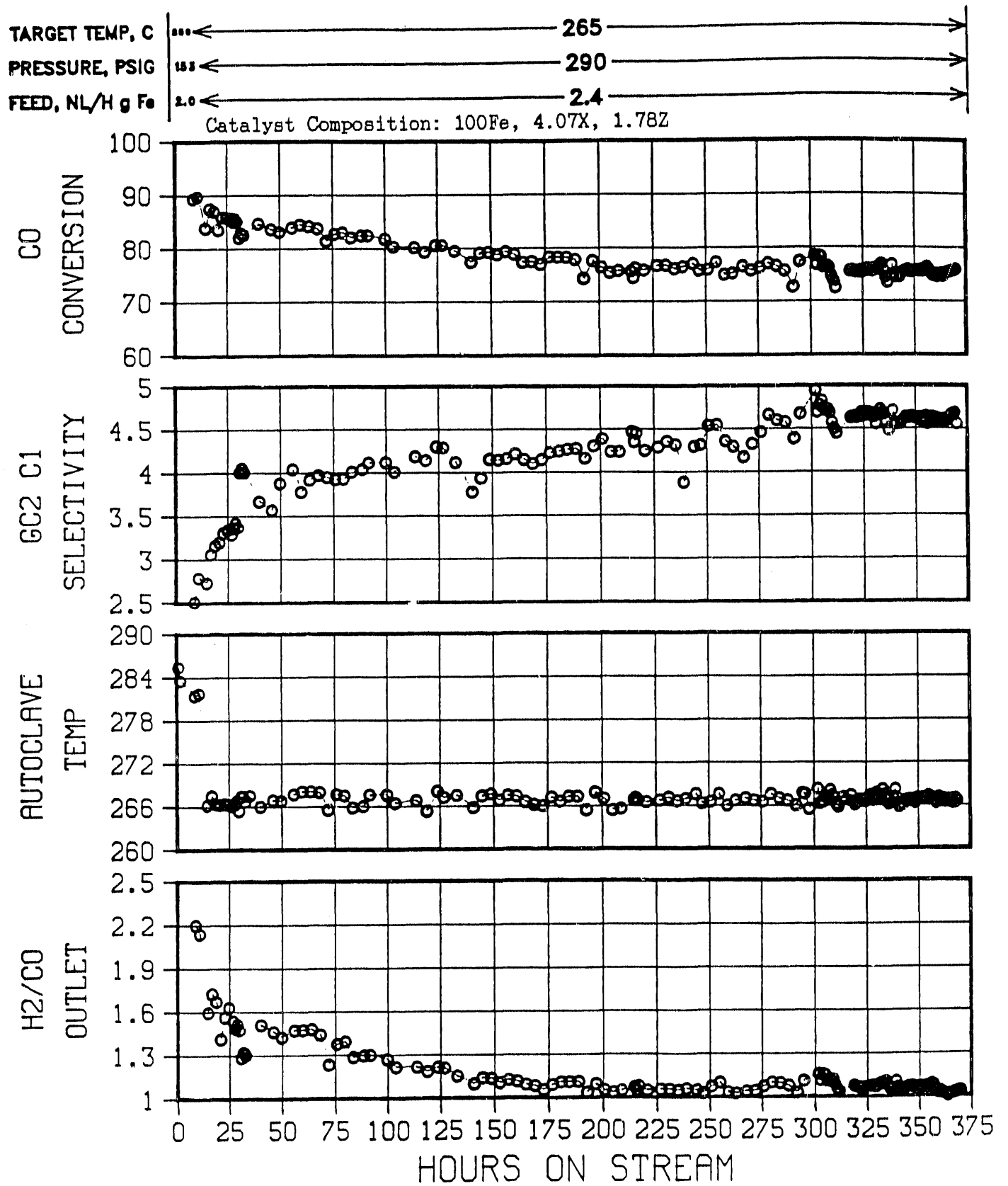
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil



PRECIPITATED IRON CATALYST 6616–49 IN SLURRY AUTOCLAVE

PLT 700B RUN 33 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R17B7 72.7g cat, 290g C_{30} oil



PRECIPITATED IRON CATALYST 6616–49 IN SLURRY AUTOCLAVE

PLT 700B RUN 33 H_2:CO feed = 0.7, 1100 rpm

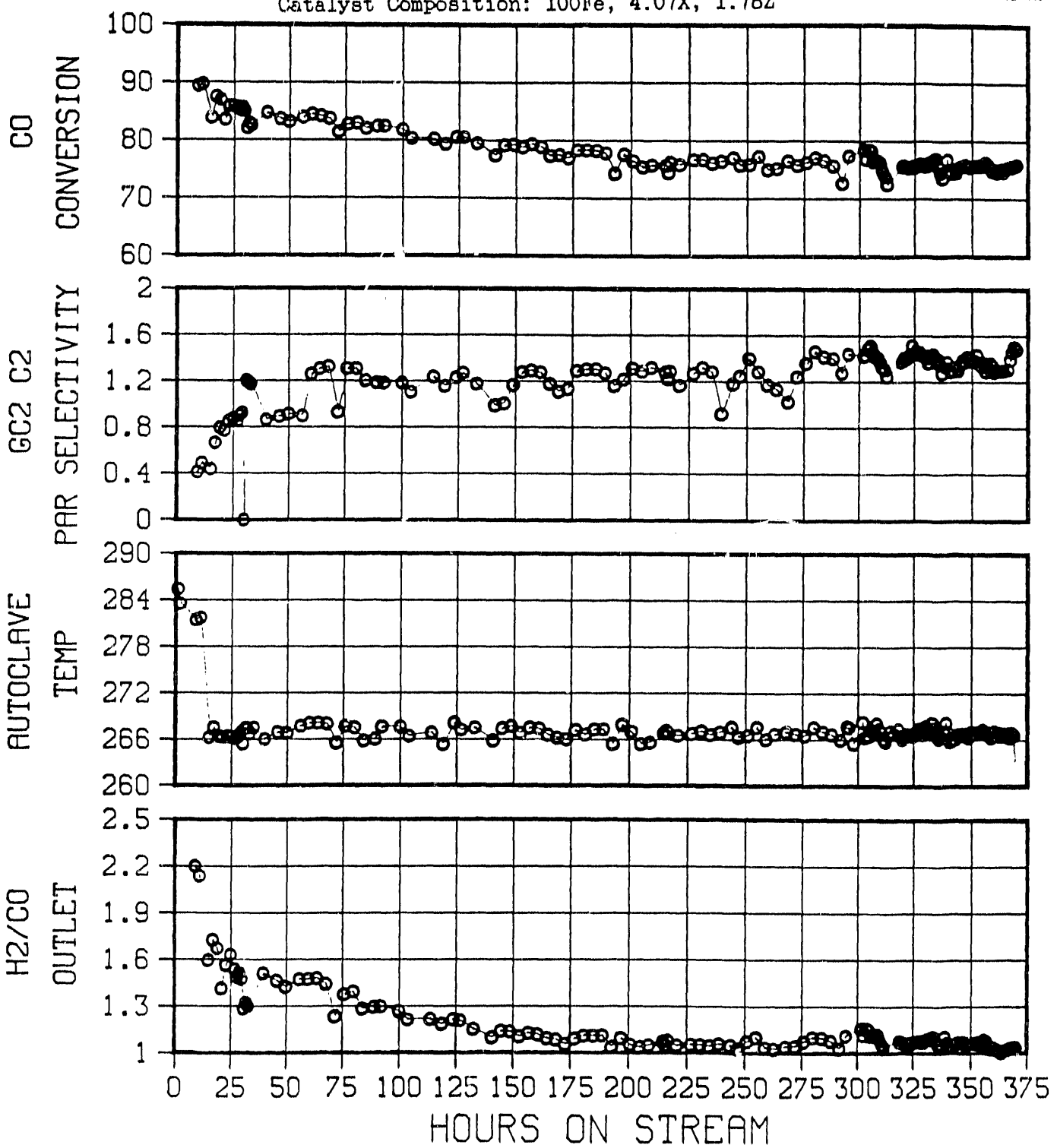
CATALYST 752R1/B7 72.7g cat, 290g C_{30} oil

TARGET TEMP, C: 265

PRESSURE, PSIG: 290

FEED, NL/H g Fe: 2.4

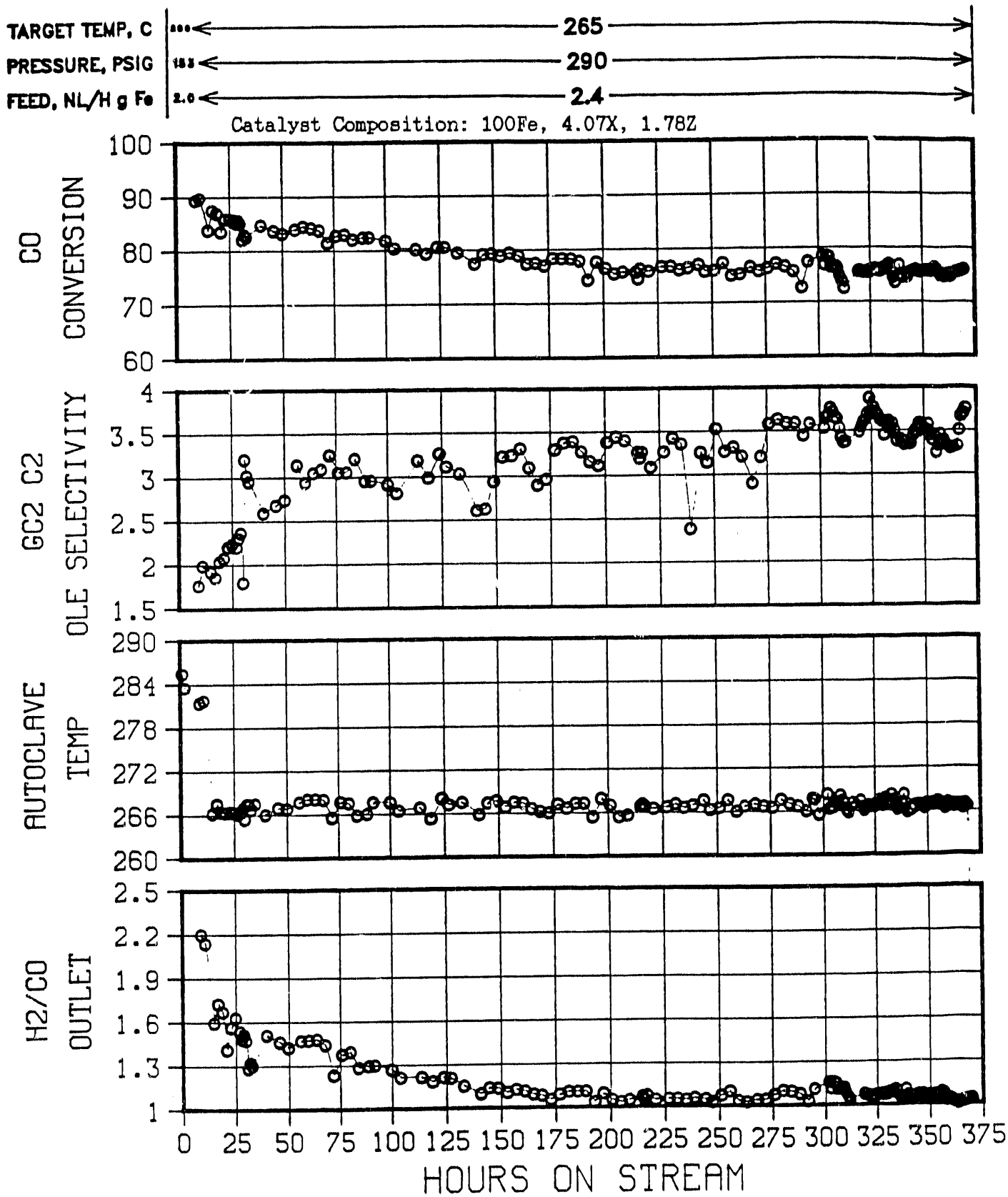
Catalyst Composition: 100Fe, 4.07X, 1.78Z



PRECIPITATED IRON CATALYST 6616–49 IN SLURRY AUTOCLAVE

PLT 700B RUN 33 H_2:CO feed = 0.7, 1100 rpm

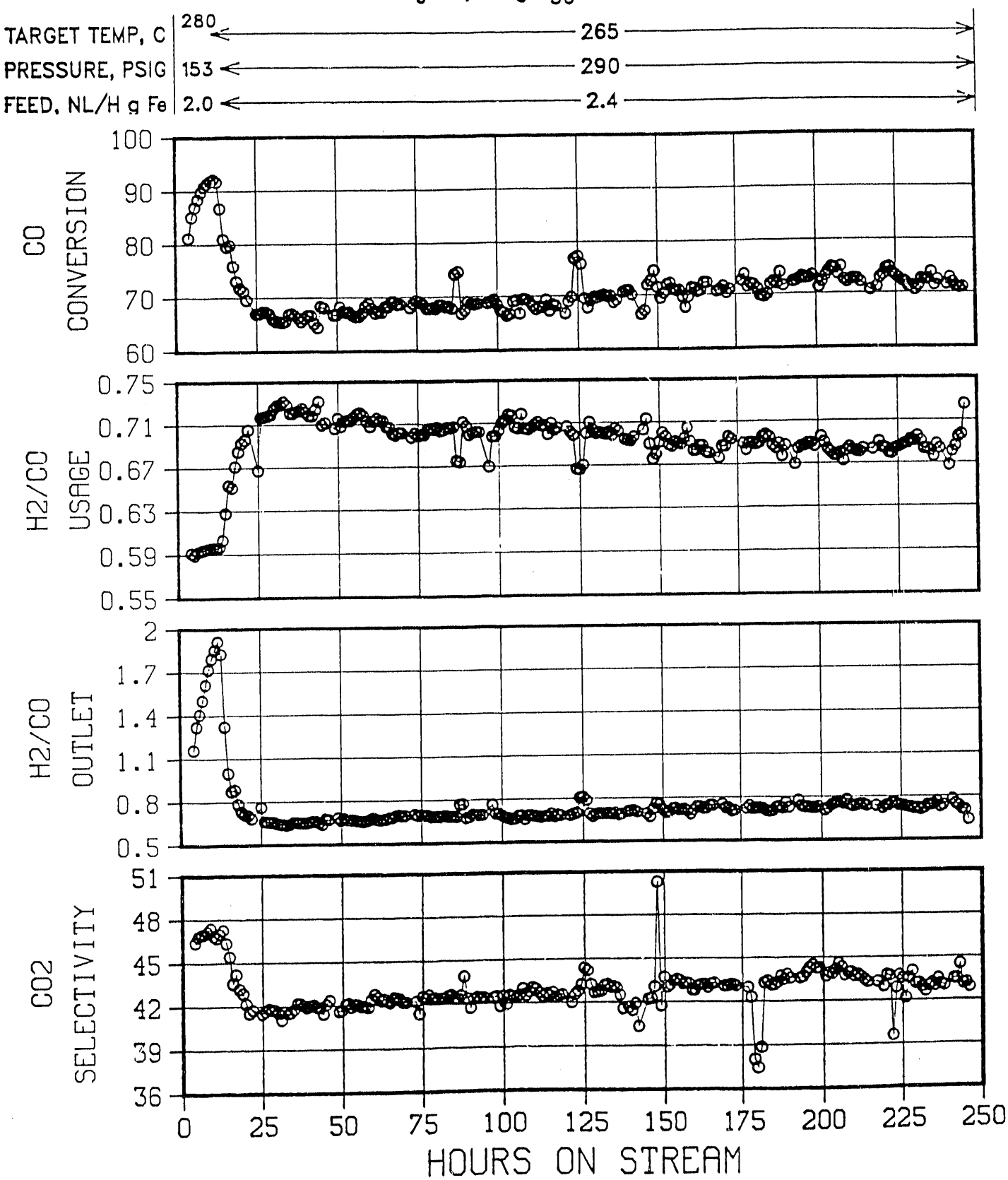
CATALYST 752R17B7 72.7g cat, 290g C_{30} oil



RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 H_2:CO feed = 0.7, 1100 rpm

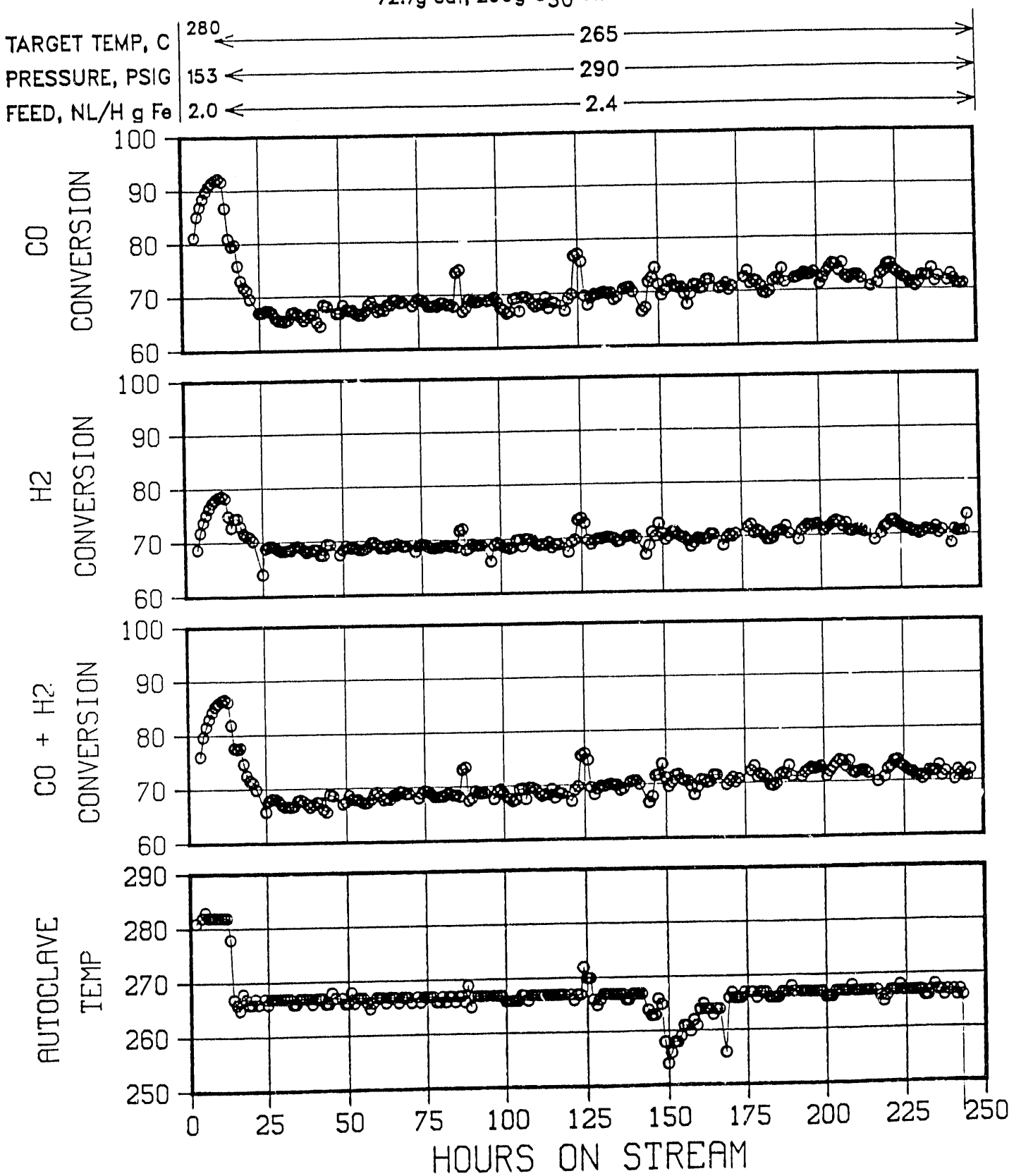
72.7g cat, 290g C_{30} oil



RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 H_2:CO feed = 0.7, 1100 rpm

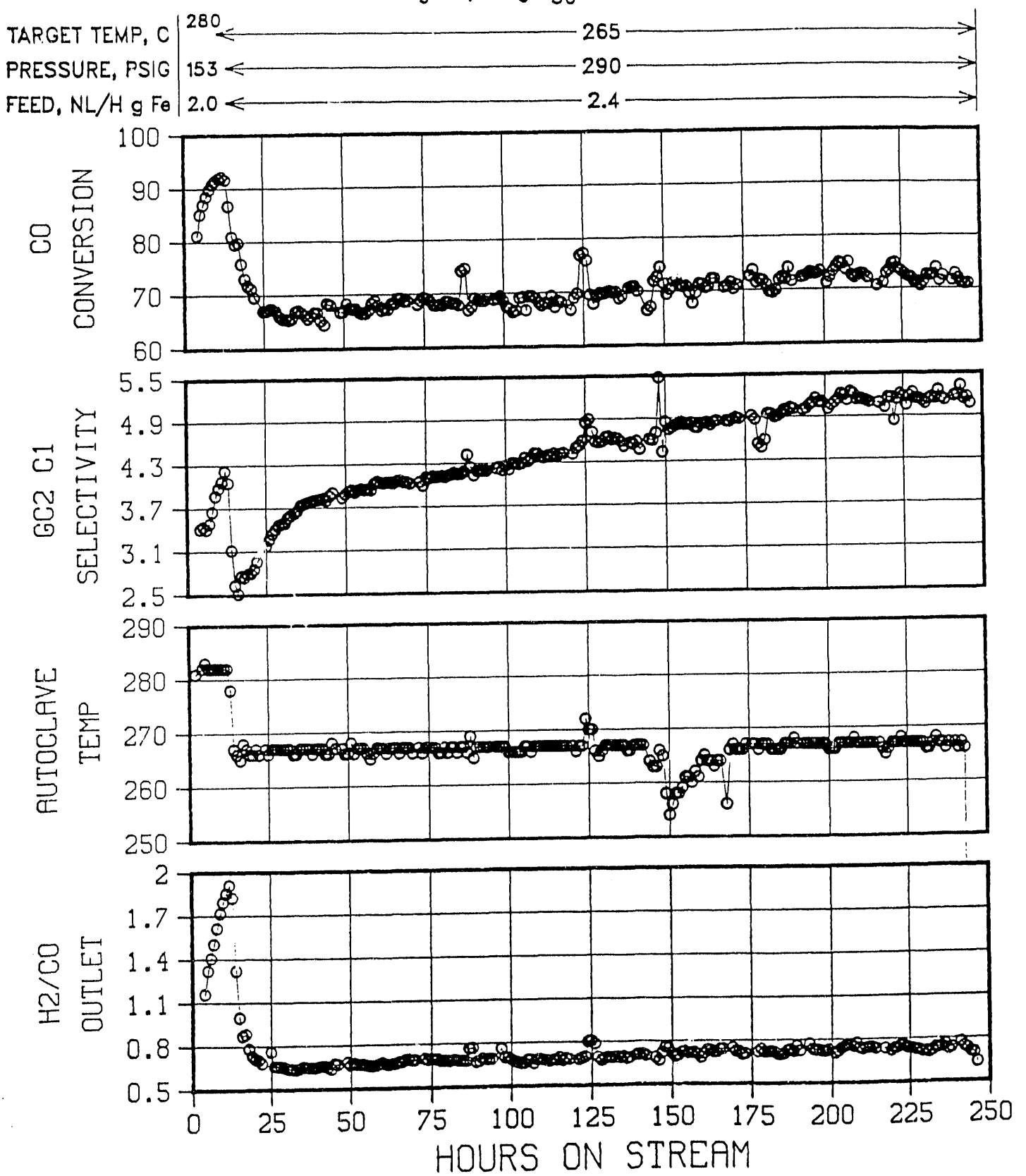
72.7g cat, 290g C_{30} oil



RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 H_2:CO feed = 0.7, 1100 rpm

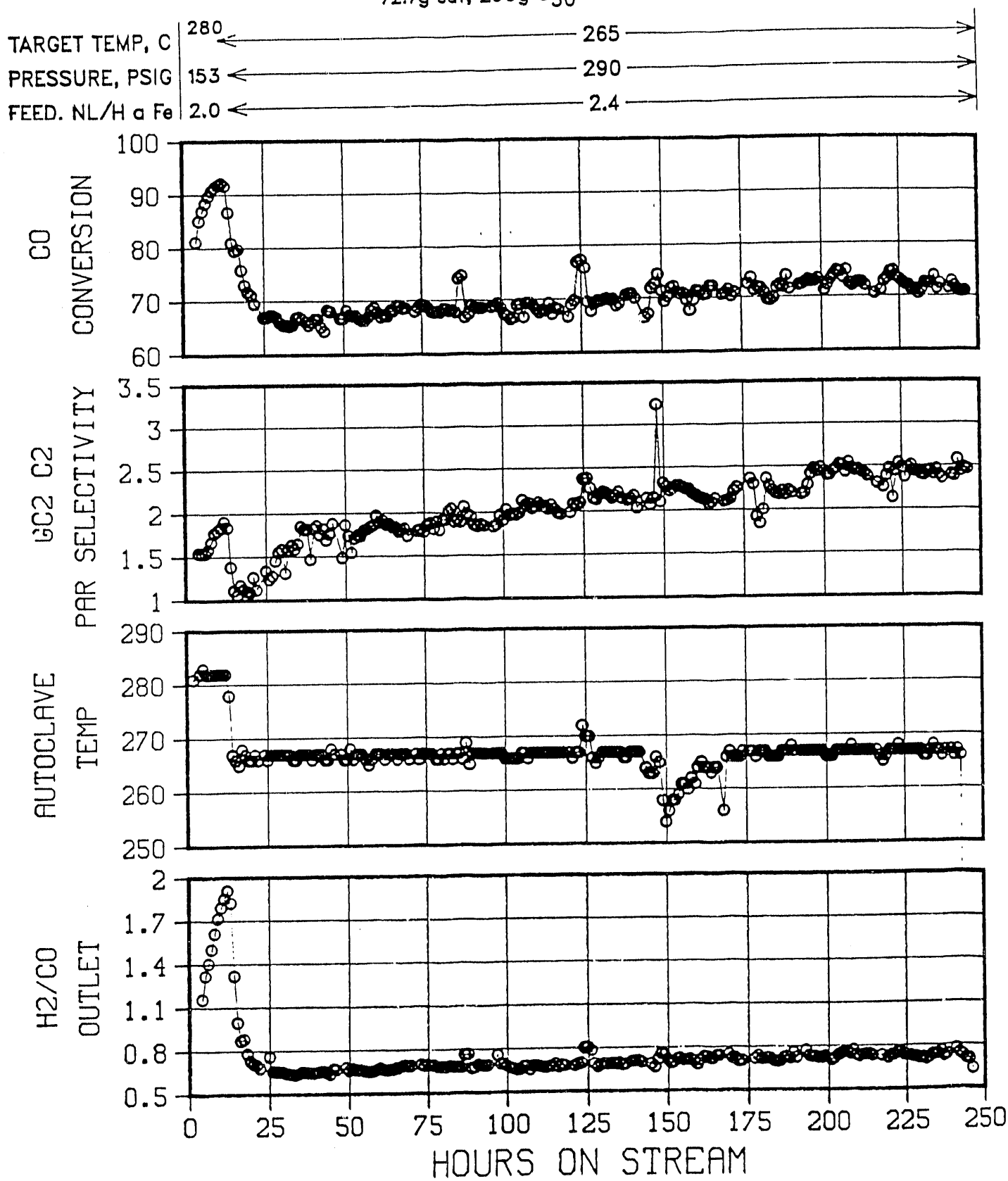
72.7g cat, 290g C_{30} oil



RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 H_2:CO feed = 0.7, 1100 rpm

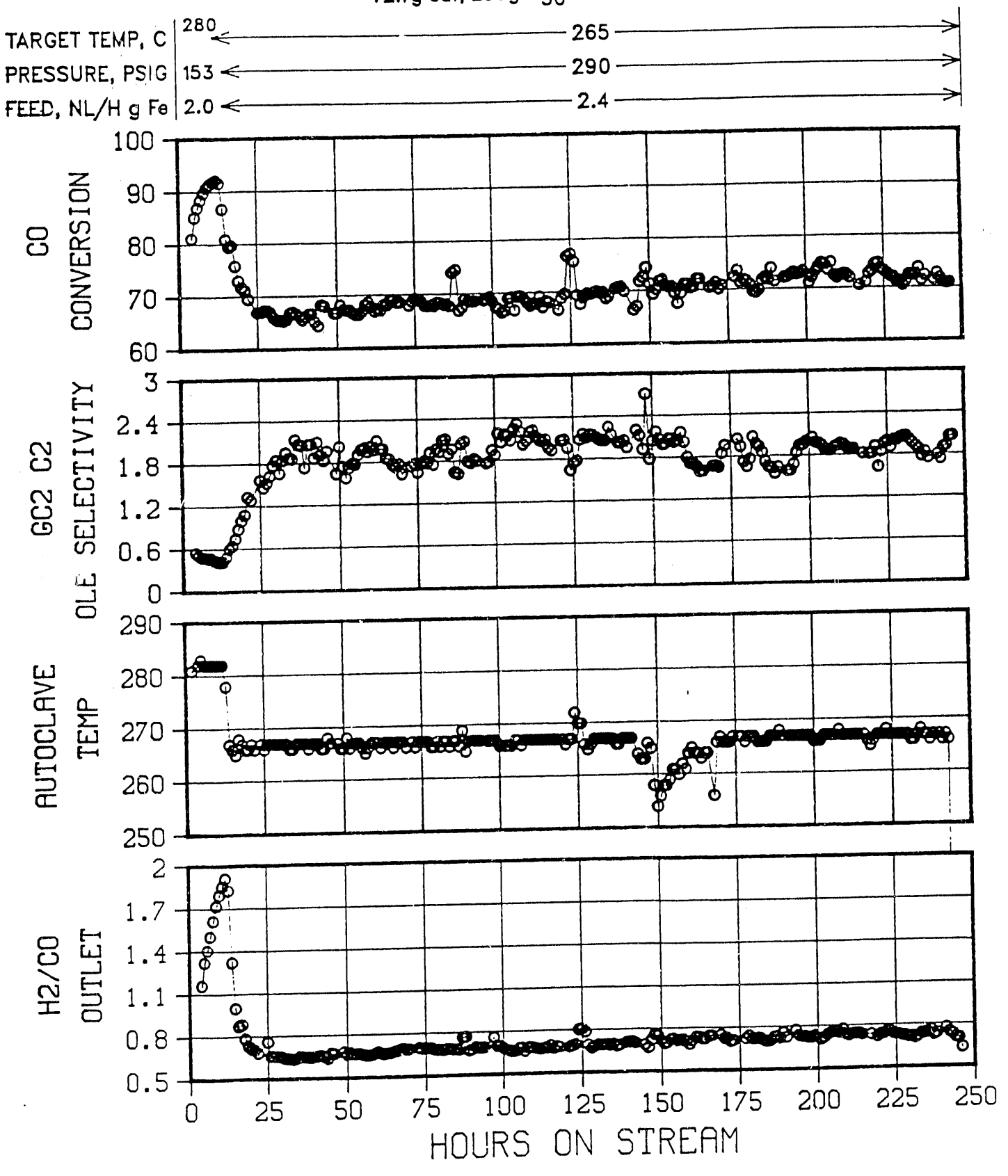
72.7g cat, 290g C_{30} oil



RUHR CHEMIE REFERENCE CATALYST

PLT 700B RUN 31 H_2:CO feed = 0.7, 1100 rpm

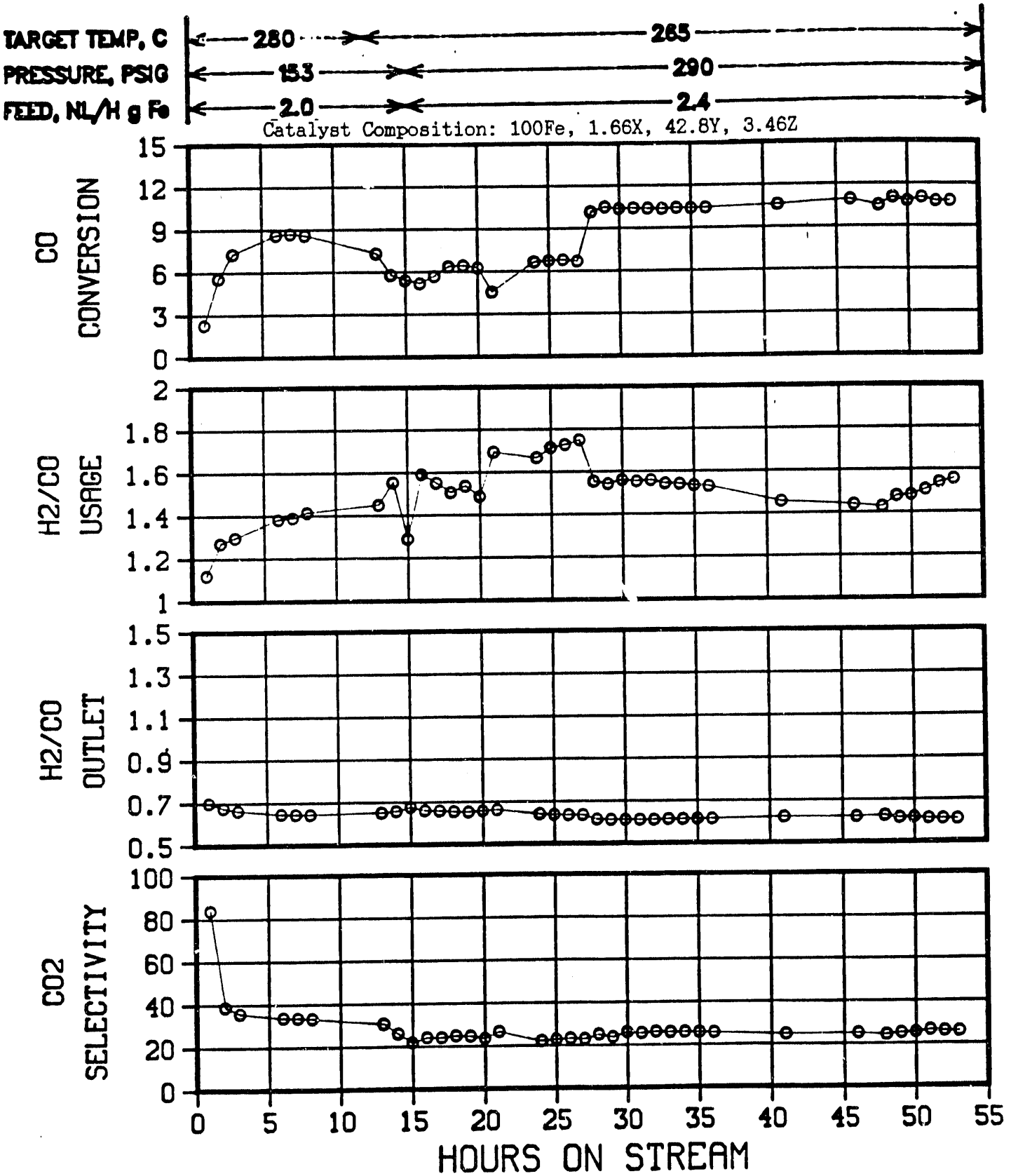
72.7g cat, 290g C_{30} oil



PRECIPITATED Fe/Si CATALYST 6616-68 IN SLURRY AUTOCLAVE

PLI 700B RUN 34 H_2:CO feed = 0.7, 1100 rpm

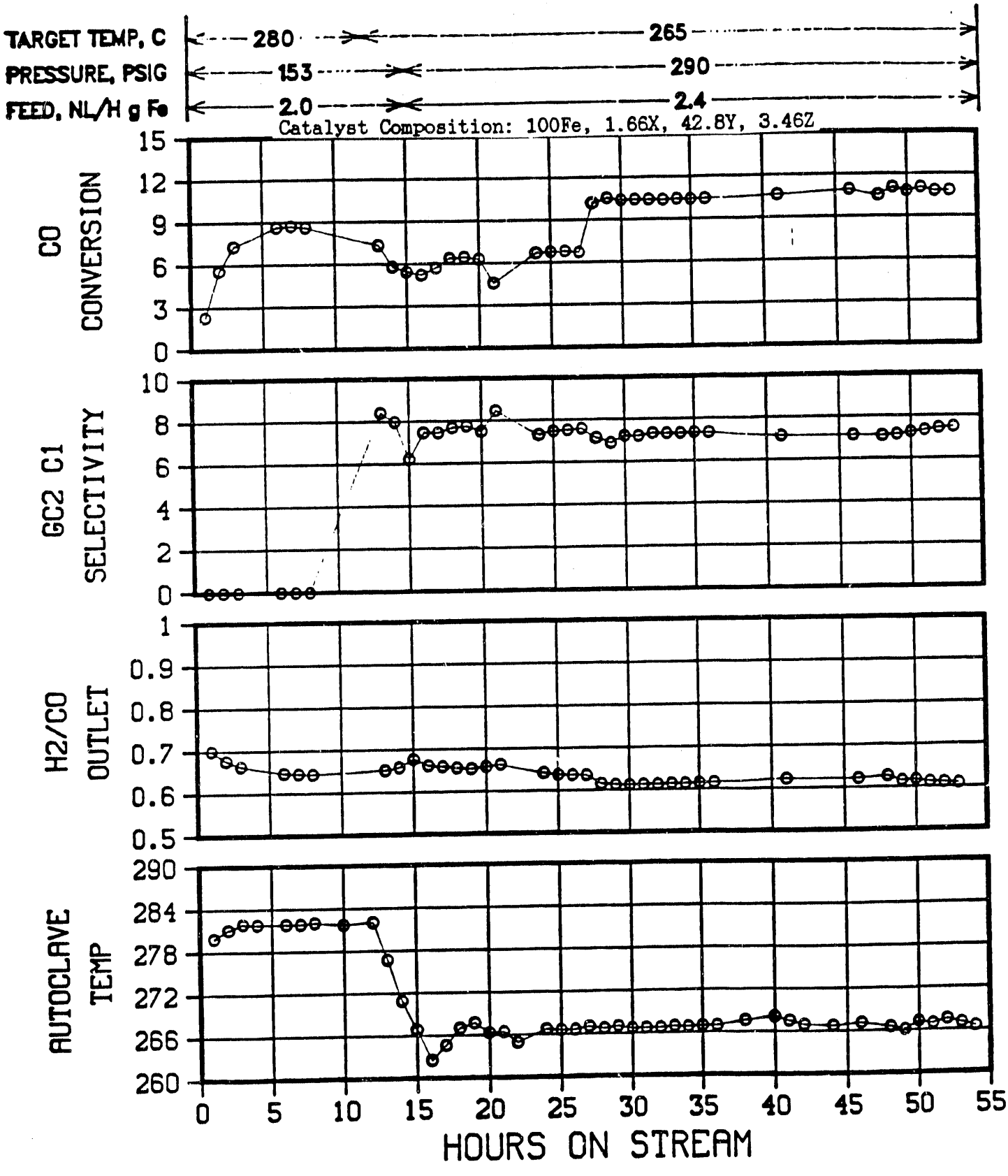
CATALYST 752R18B7 **72.7g cat, 290g C_{30} oil**



PRECIPITATED Fe/Si CATALYST 6616-68 IN SLURRY AUTOCLAVE

PLT 700B RUN 34 H_2:CO feed = 0.7, 1100 rpm

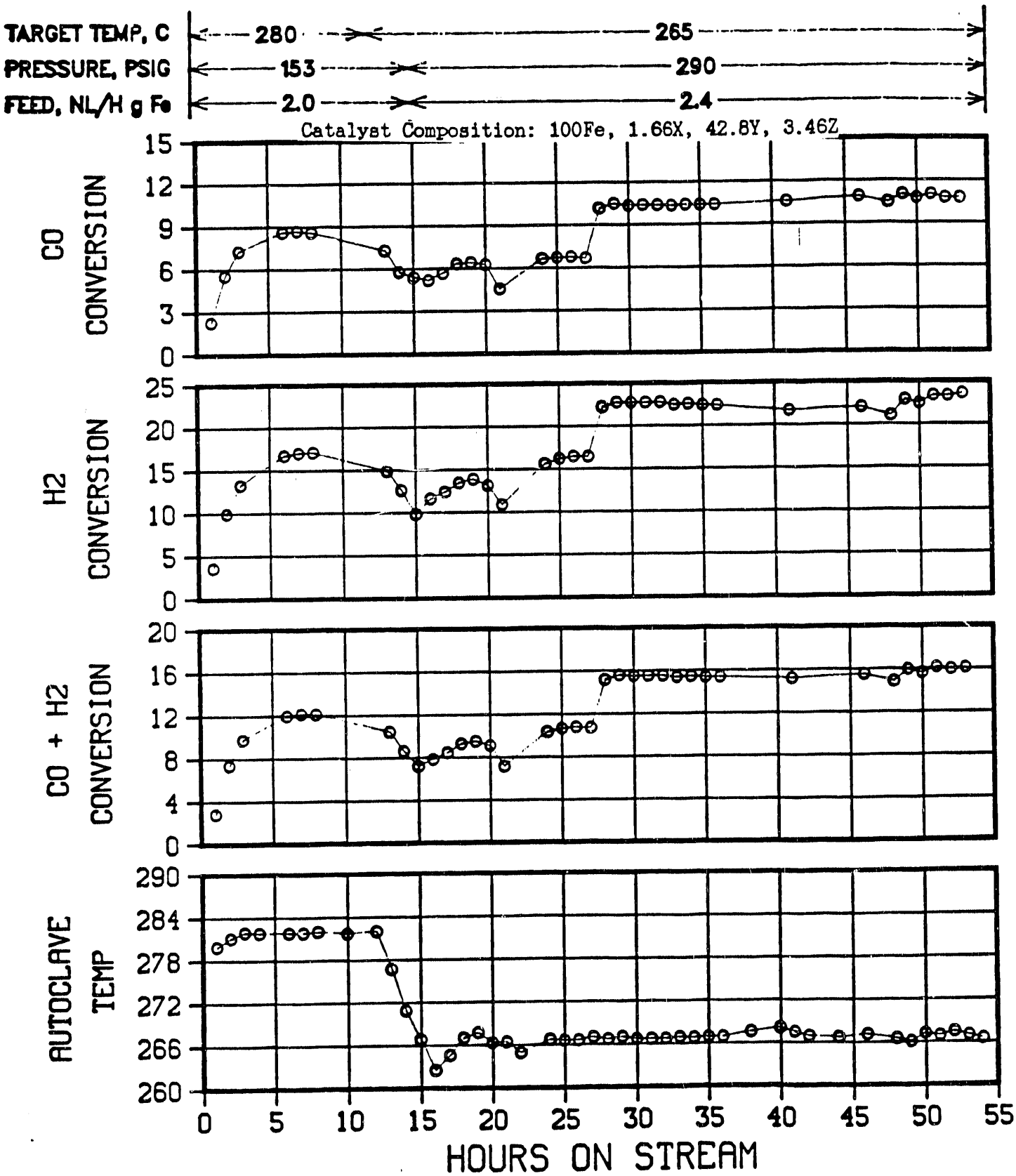
CATALYST 752R18B7 **72.7g cat, 290g C_{30} oil**



PRECIPITATED Fe/Si CATALYST 6616-68 IN SLURRY AUTOCLAVE

PLT 700B RUN 34 H_2:CO feed = 0.7, 1100 rpm

CATALYST 752R18B7 72.7g cat, 290g C_{30} oil



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4/6/92