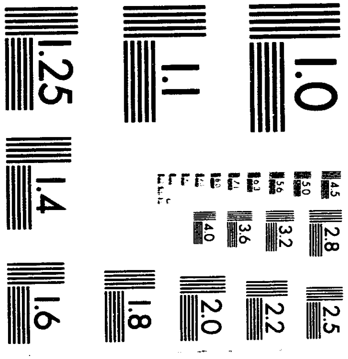
1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6

1 of 1

DOE/PC/90055--T12

TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

CONTRACT DE-AC22-90PC90055

Technical Progress Report No. 11
3/26/93-6/26/93

prepared for

Pittsburgh Energy Technology Center
Department of Energy
Pittsburgh, Pennsylvania

prepared by

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PATENT CLEARED BY CHICAGO
OPC ON March 7, 1994.

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TECHNOLOGY DEVELOPMENT FOR IRON FISCHER-TROPSCH CATALYSTS

Contract DE-AC22-90PC90055

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Technical Progress Report No. 11
(3/26/93-6/26/93)

Contract Objective

The objectives of this contract are to develop a technology for the production of active and stable iron (Fe) 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 hydrogen (H_2) and carbon monoxide (CO) in the molar ratio of 0.5 to 1.0 to the slurry bubble-column reactor, the catalyst performance target is 88% $CO+H_2$ conversion at a minimum space velocity of 2.4 NL/hr/g Fe. 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

Experimental

A slurry autoclave pilot plant is used for catalyst evaluations, the autoclave of which is contained in a 130°C hot box. The liquid and gaseous products are separately withdrawn but taken to the same traps. There are three traps in series, the first is in the hot box, the second and third are outside of the hot box and maintained at ice and dry ice/acetone temperatures respectively. A small slipstream of the product before the ice trap is taken to a GC (GC-1) for an online boiling point type of analysis. A second slipstream (after the ice trap) is taken to a second GC (GC-2) for an analysis for gases (C_1-C_4).

Scope of the Work during the Reporting Period

Task 1.3

Control of selectivity during Fischer-Tropsch processing is very important. For iron-catalyzed Fischer-Tropsch processing, potassium is used to control both activity and selectivity. In Quarterly Report No. 9 of this contract a new way of adding potassium was described. In this previous work it was found that potassium laurate could be added to the iron/copper oxide catalyst along with startup oil before a run or it could be added in solution during a run. In either case the potassium did affect the performance of the catalyst. In general, it was found that potassium-laurate-activated catalysts were less active than ones activated by the more traditional potassium carbonate impregnation/calcination method. However, the potassum laurate-activated catalysts were less selective for methane + ethane even when compared at the same conversion with the conversion being increased by lower feed rate or higher temperature.

In this report results with two other potassium salts are described. These were similar to potassium laurate in being the potassium salts of organic acids, but exhibited different behavior.

Run 63

The iron/copper oxide catalyst precursor used in this run contained one gram of potassium per 100 grams of iron. The potassium resulted from aqueous impregnation with potassium carbonate followed by calcination. Properties of the oxide are shown in Table 1. During this run a solution of potassium nonylphenolate was added to activate the catalyst and reduce light ends selectivity. Plots of conversions and selectivities as a function of hours-on-stream are in Appendix 1 as Figures A-1 to A-10. The response to this addition, however, was not the same as that of a similar catalyst to addition of potassium laurate (Quarterly Report No. 9, this contract). At a later time during this run a solution of potassium laurate was added and the response expected for this salt was observed.

The two organic potassium salts used in Run 63 were dissolved in the same solvent system, namely, 50/50 heptane/isopropanol (weight). Although the potassium nonylphenolate was more soluble than the potassium laurate, the two salts were dissolved to the same weight percent. The periodic additions of potassium nonylphenolate were started at ninety hours-on-stream (Figure A-2). These additions began at a time when the catalyst appeared to be near line out in conversion (CO conversion = 37%). By the end of the potassium nonylphenolate additions the total amount of potassium added was 2.3 g/100 g of iron. This can be compared to the previous Run 49 which used an iron/copper oxide containing the same amount of potassium carbonate-derived potassium, but a solution of potassium laurate instead of potassium nonylphenolate. During Run 49 the total amount of potassium added (from potassium carbonate and potassium laurate) at 250 hours on stream was 2.4 g/100 g of iron. At this time the CO conversion was 70% vs. 46% in Run 63 at 175 hours on stream after addition of the same total amount of potassium but from potassium carbonate and potassium nonylphenolate. At similar times on stream the methane selectivities were 3.1 mol% for Run 49 and 5.0 mol% for Run 63. Therefore, potassium nonylphenolate did not affect either conversion or light hydrocarbon selectivity as strongly as potassium laurate.

At 230 hours-on-stream during Run 63 a solution of potassium laurate was started. An immediate sharp gain in conversion and sharp reduction in light ends selectivity resulted.

Table 2 compares catalyst performance in Runs 49 and 63 after the addition of 3.0 g potassium/100 g of iron. Up to this time the operating conditions during both runs, including activation procedure, were the same, and the data presented are from approximately the same times on stream. Two different sources of potassium had been used for the additions during Run 63, nevertheless, the Run 49 and Run 63 conversions in Table 2 are about the same. However, the Run 49 methane + ethane selectivity (3.4 mol%) was lower than that from Run 63 (4.9 mol%). This difference is largely due to the difference in ethane selectivity, which in turn is possibly due to the Run 63 catalyst being more active for hydrogenation of ethylene. Since a low methane + ethane selectivity is critical for the objectives of this project, this is an important observation.

Potassium laurate was superior to potassium nonylphenolate but the possibility exists that compounds even better than potassium laurate can be found. Based only on the results with the two compounds above it is hard to predict what compound might be superior. However one might guess that other potassium carboxylate(s) might be found that are superior to potassium laurate. There are many potassium carboxylates available with varying steric and electronic properties.

Run 65

In this run only twenty-five grams of iron/copper oxide catalyst precursor were used. Runs described in Quarterly Report No. 10 of this contract were the first to use such a low level of oxide. Potassium was added as solid potassium benzoate at the beginning of the run and once later in the run as a solution in isopropanol. Properties of the oxide used are in Table 1. Plots of conversions and selectivities as a function of hours-on-stream are in Appendix 1 as Figures A-11 to A-17. A high percent loss in conversion during line out is a characteristic of runs with low catalyst loading, for instance, see Figure A-12. Two reference runs (Runs 56 and 58) with iron oxides containing startup potassium from, respectively, potassium carbonate and potassium laurate are described in the earlier Report No. 10. Solutions of potassium salts were not added during these runs. The operating conditions, including catalyst activation, were the same in all three runs. Performance data from Runs 56, 58 and 65 at 100 hours-on-stream are compared in Table 3. There was a different rate of deactivation in the three runs, but all lined out at conversions below the 100 hours-on-stream conversion. The selectivity conclusions made by comparing the 100 hours are valid at all times on stream. The Run 56 catalyst was intrinsically more selective to methane than the Runs 58 and 65 catalysts, however, the Run 65 catalyst was more selective to ethane than the Run 56 catalyst with the result that these two catalysts, which were of about the same activity, also had about the same methane + ethane selectivity.

The most surprising observation during Run 65 was that addition of potassium benzoate solution during the run produced only a slight increase in conversion but notable increases in all C_1-C_4 hydrocarbons. In all other work during this contract increased potassium resulted in decreased light ends selectivities. The addition of potassium benzoate which began at 275 hours-on-stream only increased the total potassium level from 1.8 g/100g iron to 2.9 g/100 g iron. This latter number is not high compared to any of the previous runs in this contract and cannot, therefore, be used as an explanation for the unusual selectivity observations.

Addition of solid potassium benzoate at the beginning of a run with iron/copper oxide resulted in a catalyst of similar activity to one prepared from impregnation/calcination of potassium carbonate onto an iron/copper oxide. Both catalysts were more active than one prepared through addition of solid potassium laurate with iron/copper oxide at the beginning of a run. Although lower methane selectivity was noted for the potassium benzoate catalyst than the potassium carbonate one, the potassium carbonate one was less selective for ethane. This latter observation is possibly due to a lower rate of ethylene hydrogenation by the potassium carbonate catalyst.

Addition of potassum benzoate during Run 65 resulted in **higher** not lower light hydrocarbon selectivities, the opposite was expected based on results with potassium laurate or potassium nonylphenolate addition during a run. The reason for this difference is unclear; it means that the potential of using potassium benzoate to meet the objective of this contract is low. However, it is possible that further, hopefully useful, activity/selectivity effects will be observed with other organo-potassium compounds.

Conclusions

Besides potassium carbonate, three different potassium-containing molecules have now been evaluated for modifying the behavior of iron-based Fischer-Tropsch catalysts. Of these potassium laurate is the most promising for achieving the objectives of this contract which are high conversion and low methane + ethane selectivity. Additional potassium-containing molecules should be studied. For instance, other long-chain carboxylic acid salts are available as well as more complex structures such as the salts of dicarboxylic acids. Substituted benzoic acids are available which might be useful to understand the electronic, as opposed to the steric, effect. There are also many other potassium-containing molecules such as potassium alkoxides and potassium enolates which are well-characterized, differ a lot in structure from the three evaluated so far, and are easy to prepare. Finally, organic salts of other alkali metals might be used.

Plans for the Next Quarter

Additional work is contemplated to certify that the iron/copper oxide preparation plant can be routinely operated to produce high yields of acceptable catalyst precursor.

TABLE 1
CATALYST PRECURSOR PROPERTIES

PLT/RUN NO.	701/63	701/65
K ADD. METHOD	K_2CO_3 + ORG K SALTS[1]	K BENZOATE
CATALYST PRECUR., g	72.3	25
OXIDE PART		
ELEMENTAL ANAL.		
Fe, WT %	57.9	64.5
Cu, WT %	0.78	2.25
K, WT %	0.60	(2)
Fe:K, WT	1.0	1.8
NITROGEN POROS.		
SA, m^2/g	197	133
PV, cc/g	0.22	0.30
MESH RANGE	-140 +400	-140 +400
Fe:K, WT (TOTAL) AFTER K ADDITION IN SOLVENT		
AFTER K LAURATE	2.3	
AFTER K NONYLPHENOLATE	3.9	
AFTER K BENZOATE		4.0

1. SOLUTION OF K LAURATE FOLLOWED BY ONE OF K NONYLPHENOLATE.
2. K ADDED AS SOLID K BENZOATE AT BEGINNING WITH THE Fe/Cu OXIDE.

TABLE 2
RUN 49 VS. RUN 63

RUN NO.	49	63
g K/100 g Fe	3.0	3.0
HRS ON STREAM	300	270
CO CONVERSION, %	70	68
SELECTIVITIES, MOLE %		
C_1	2.6	2.9
C_2	0.8	2.0
$C_2^=$	2.1	0.7
C_3	0.6	0.5
$C_3^=$	3.8	3.0
C_4	0.6	0.0
$C_4^=$	2.8	2.5

TABLE 3
RUNS 56 AND 58 VS. RUN 65

RUN NO.	56	58	65
SOURCE OF POTASSIUM	K_2CO_3	K LAURATE	K BENZOATE
g K/100 g Fe	2.1	2.1	1.8
HRS ON STREAM	100	100	100
CO CONVERSION, %	53	30	50
SELECTIVITIES, MOLE %			
C_1	4.7	2.0	3.0
C_2	1.4	0.0	2.9
$C_2^{=}$	1.5	0.7	0.6
C_3	1.0	0.5	0.7
$C_3^{=}$	7.0	2.9	3.7
C_4	1.1	0.0	0.0
$C_4^{=}$	5.5	2.0	2.8

FIGURE A-1

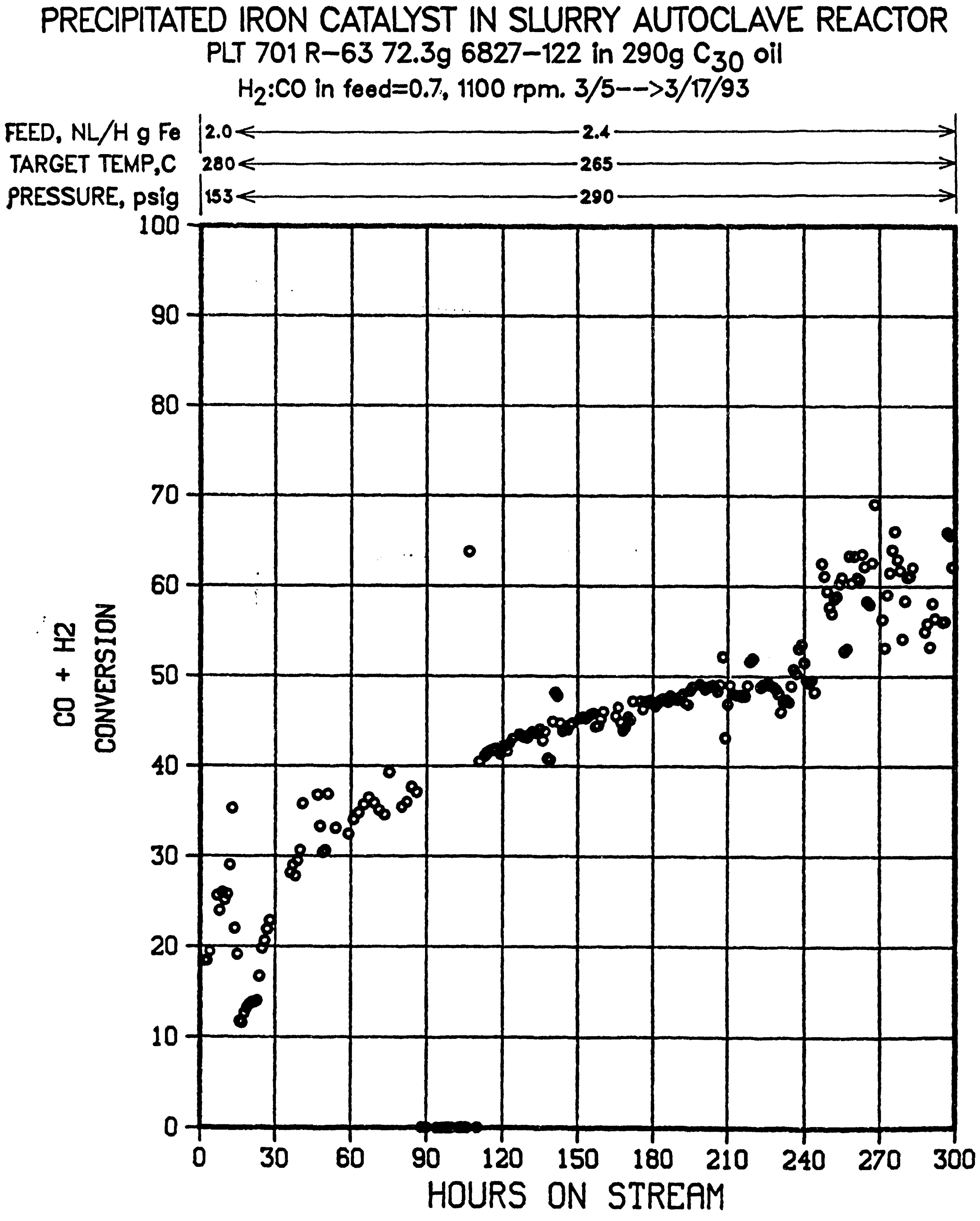

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR
PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil
H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93
FEED, NL/H g Fe
2.0
2.4
TARGET TEMP,C
280
265
PRESSURE, psig
153
290
100
90
80
70
60
50
40
30
20
10
0
CO + H2
CONVERSION
0
30
60
90
120
150
180
210
240
270
300
HOURS ON STREAM

FIGURE A-2

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R-63 72.3g 6827-122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

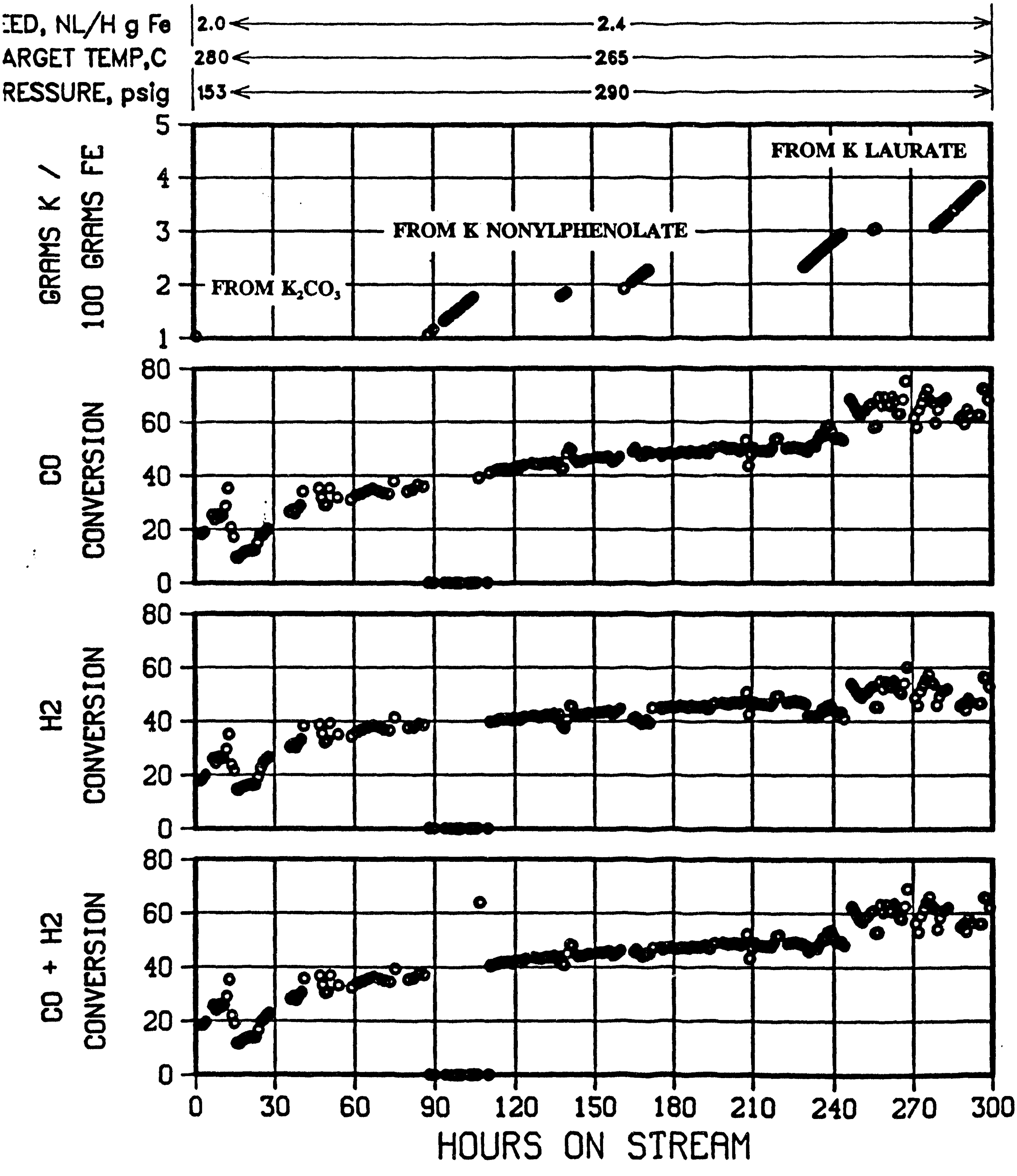


FIGURE A-3

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

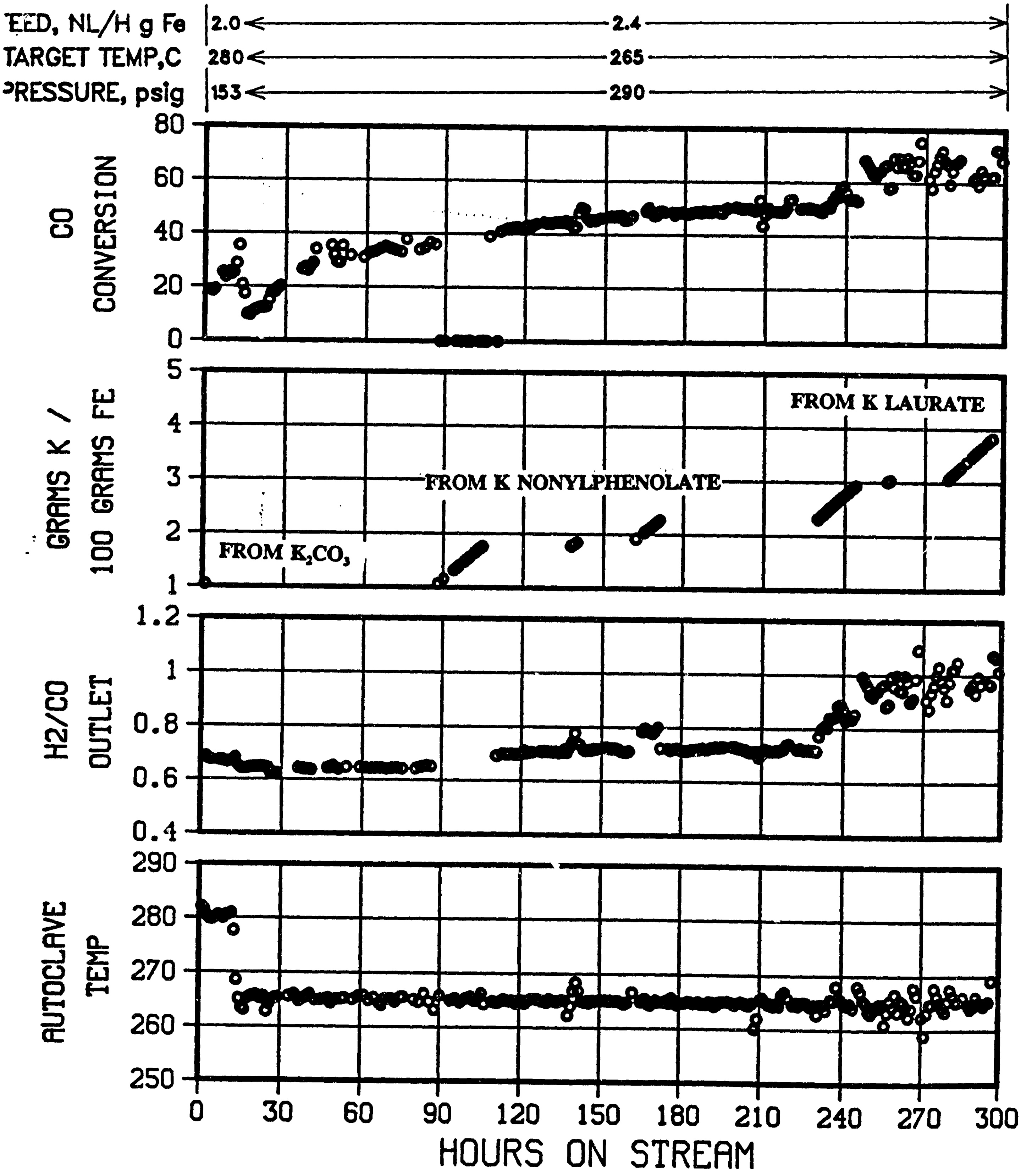


FIGURE A-4

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR
PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil
H_2:CO in feed=0.7, 1100 rpm. 3/5-->3/17/93

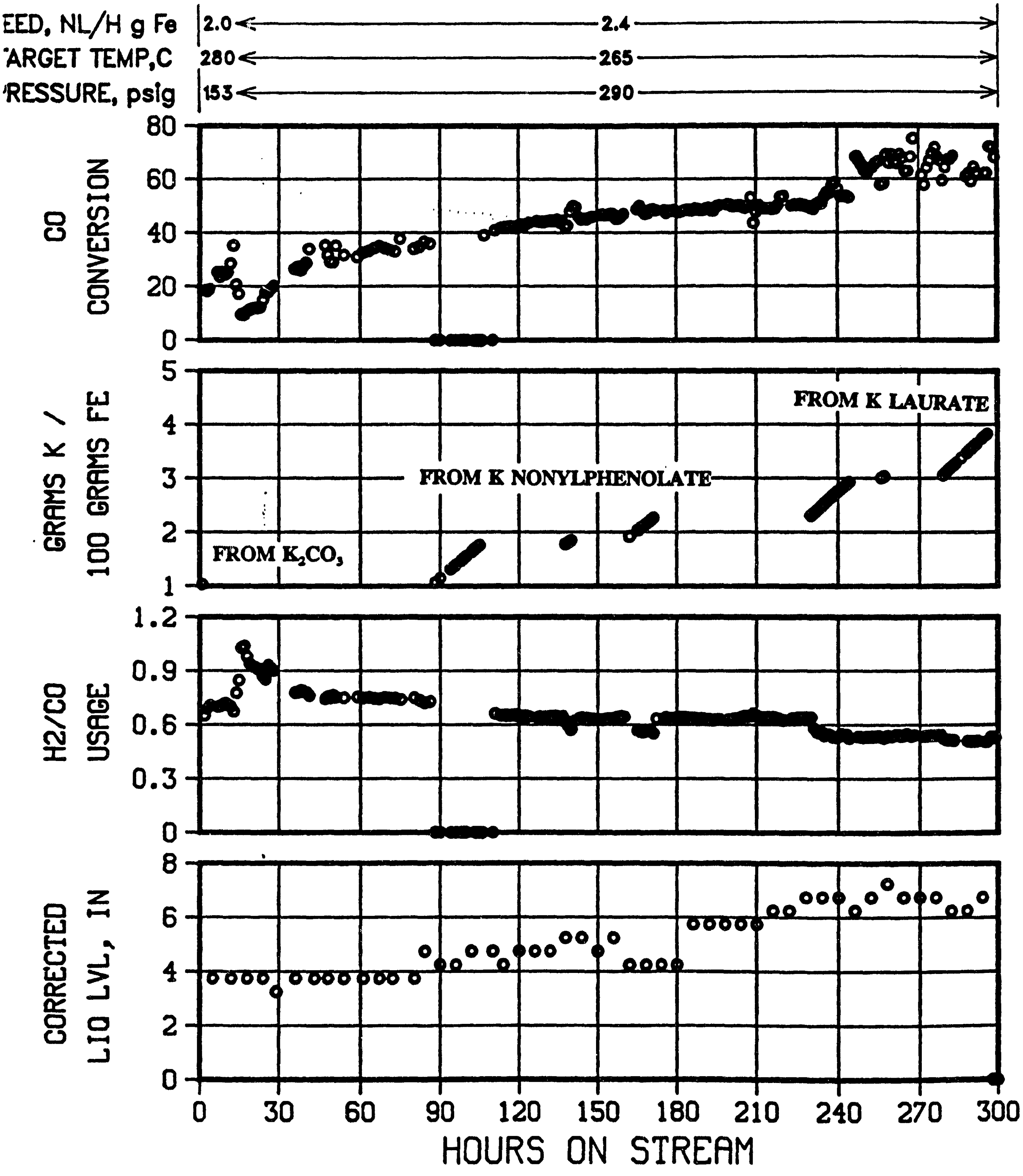


FIGURE A-5

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93

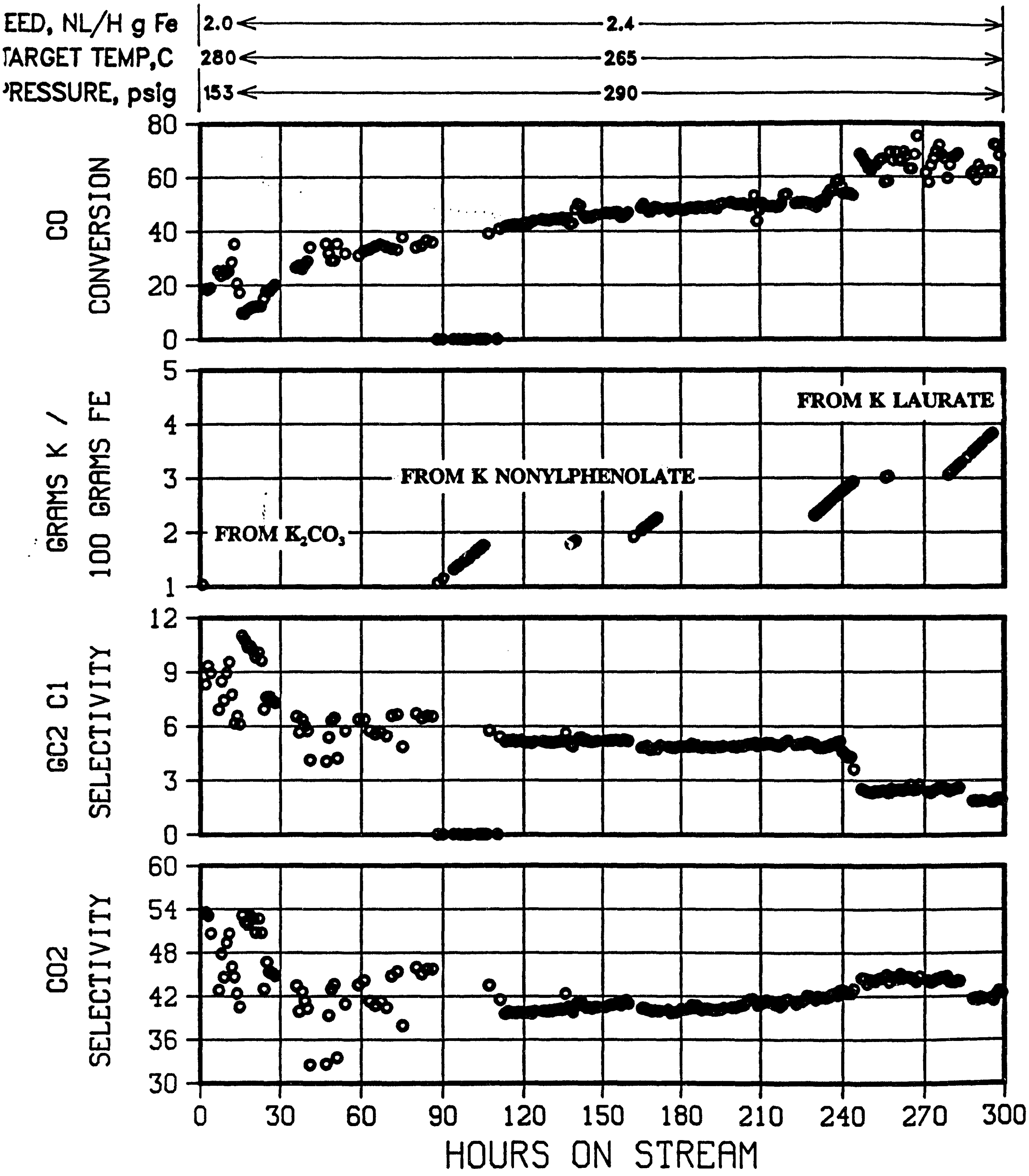


FIGURE A-6

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR
PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil
H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93

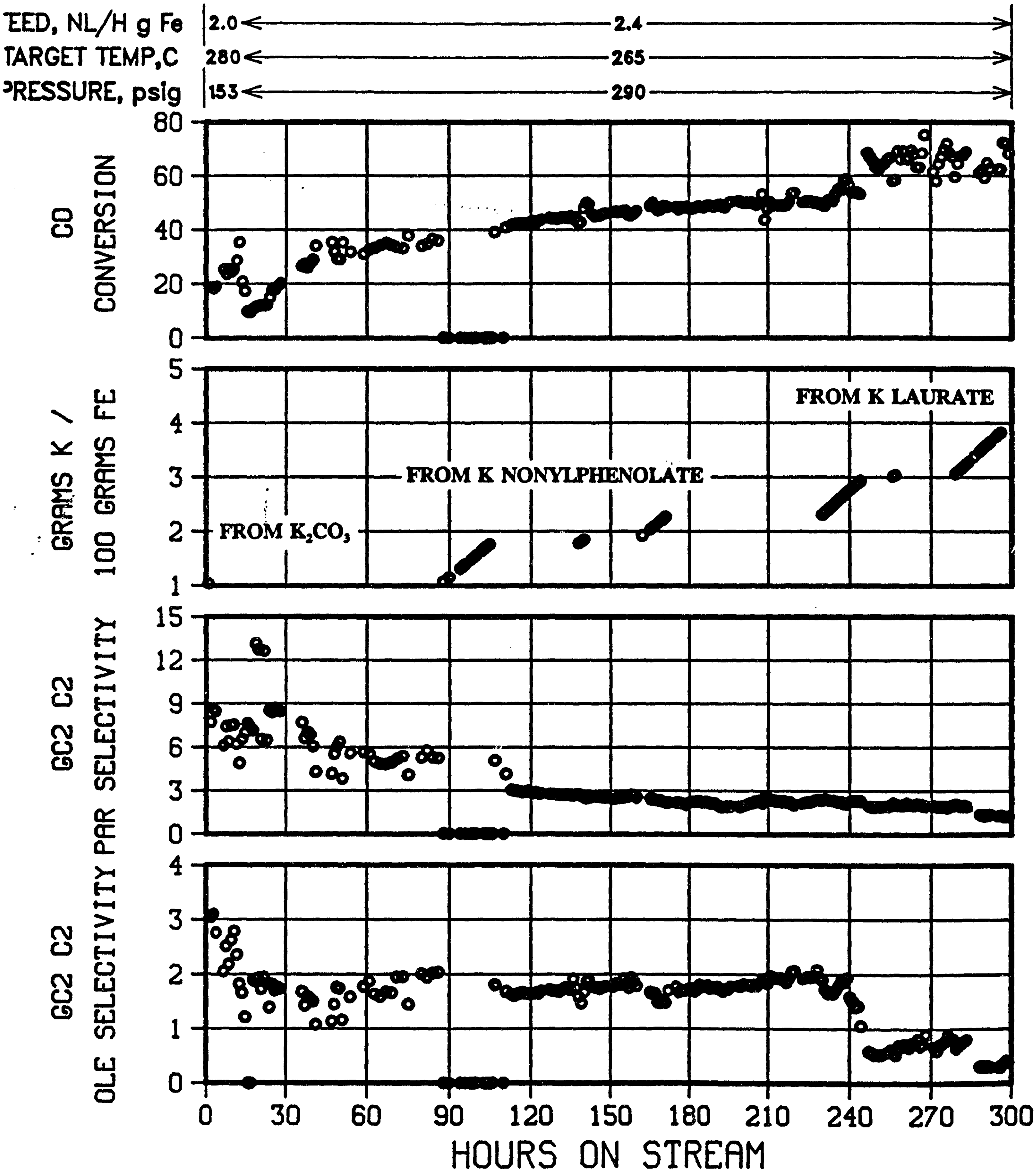


FIGURE A-7

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93

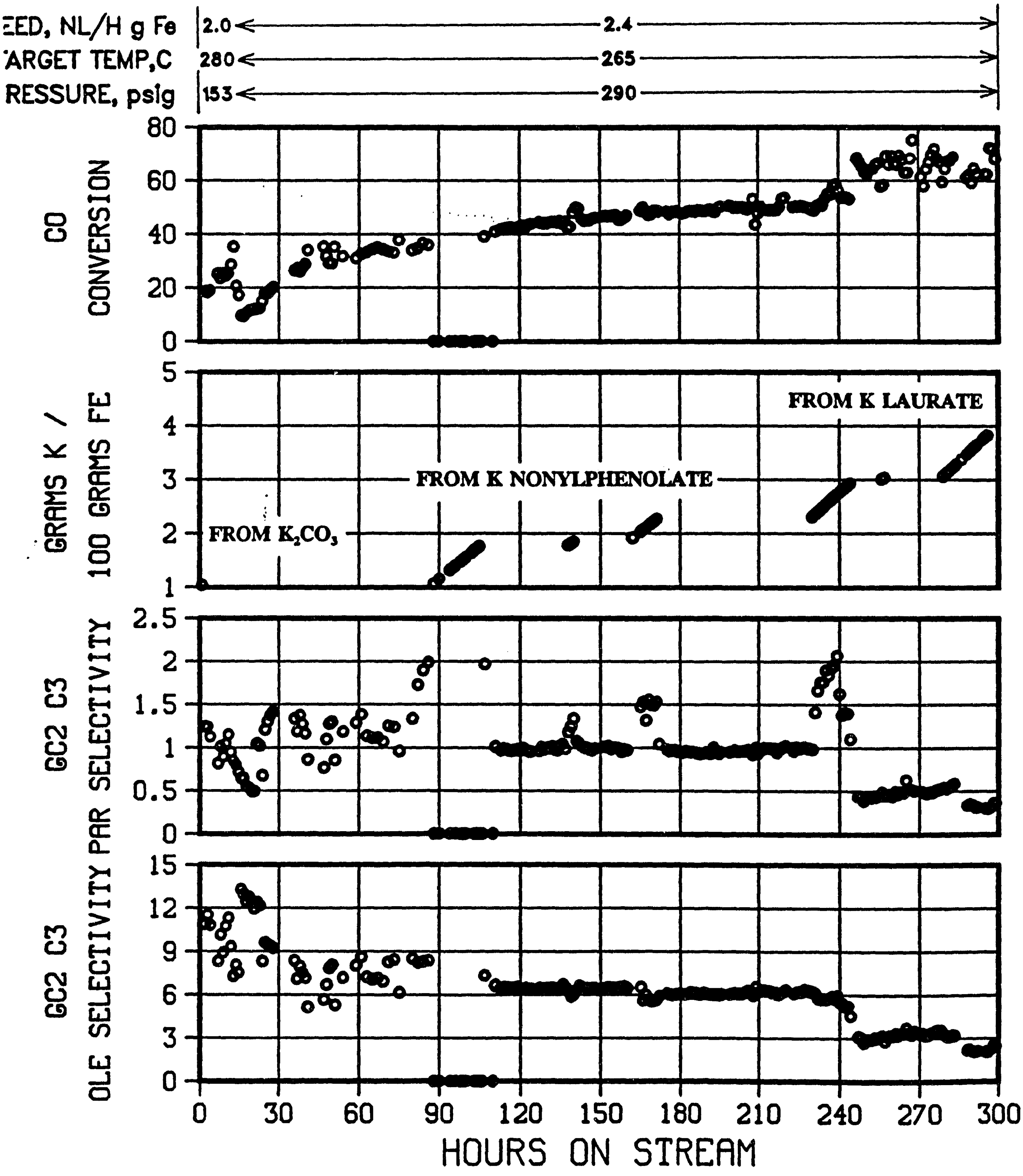


FIGURE A-8

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R−63 72.3g 6827−122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5−−>3/17/93

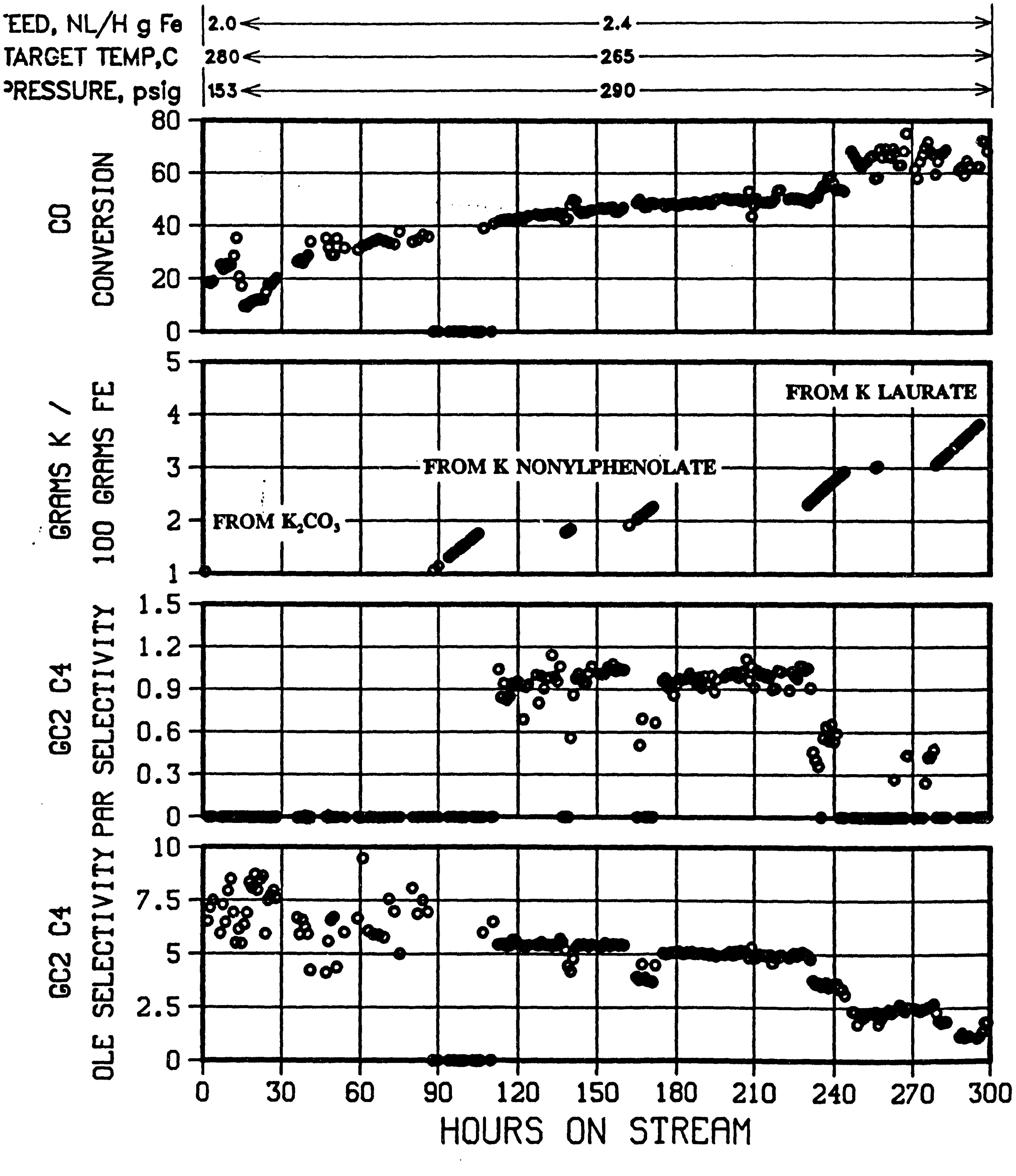


FIGURE A-9

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93

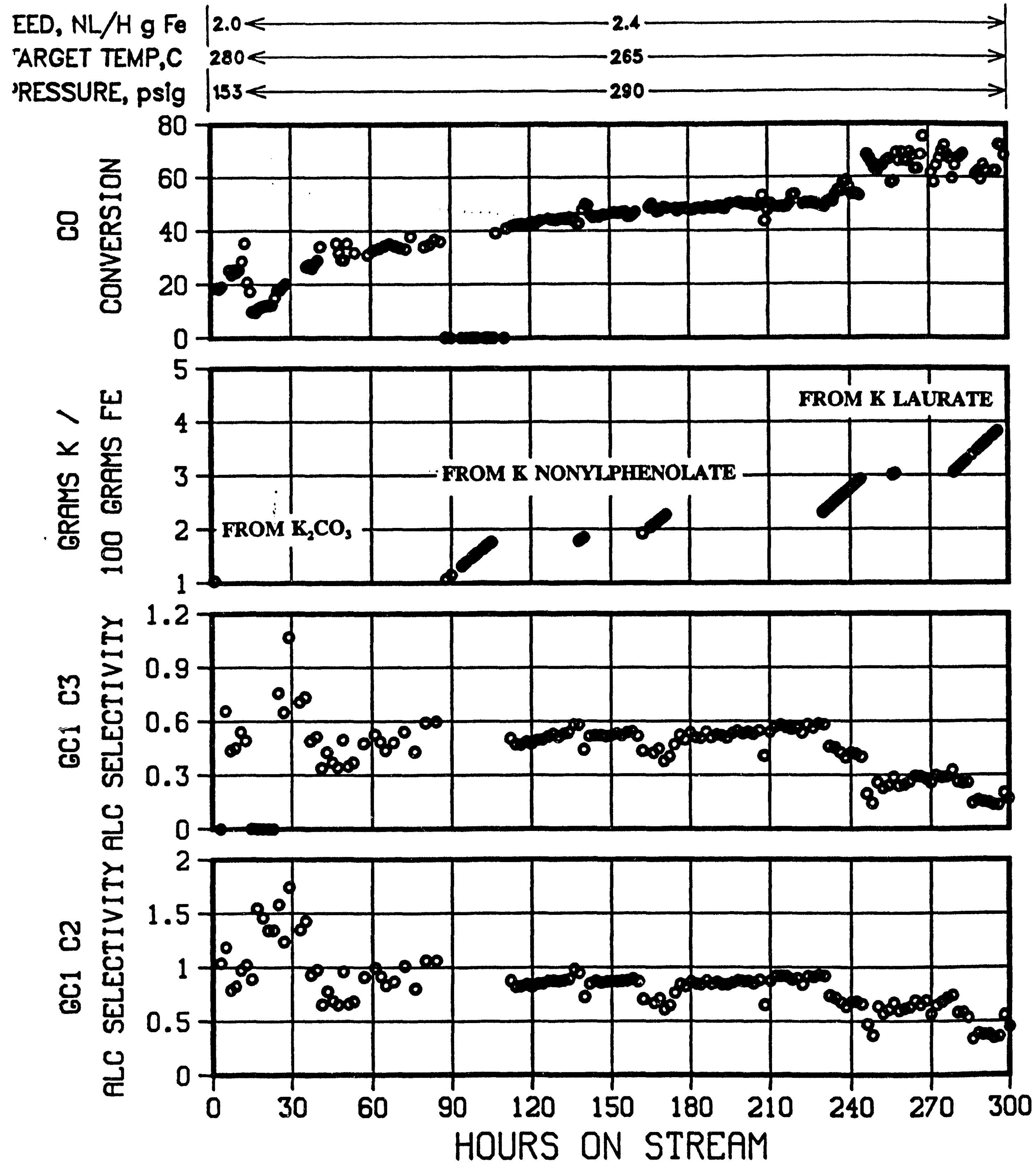


FIGURE A-10

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLT 701 R–63 72.3g 6827–122 in 290g C_{30} oil

H_2:CO in feed=0.7, 1100 rpm. 3/5––>3/17/93

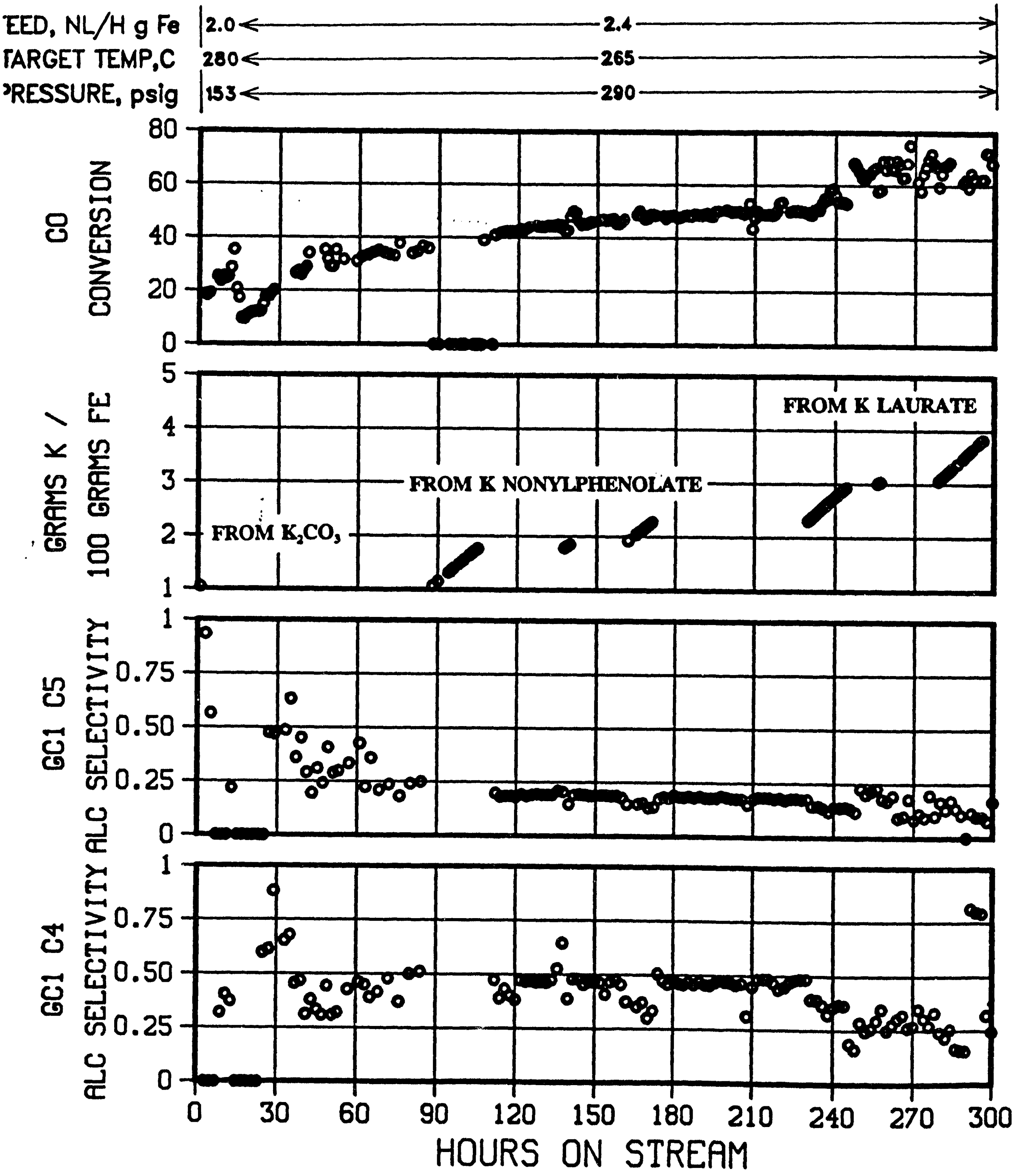


FIGURE A-11

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C$_{30}$ oil

H_2:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

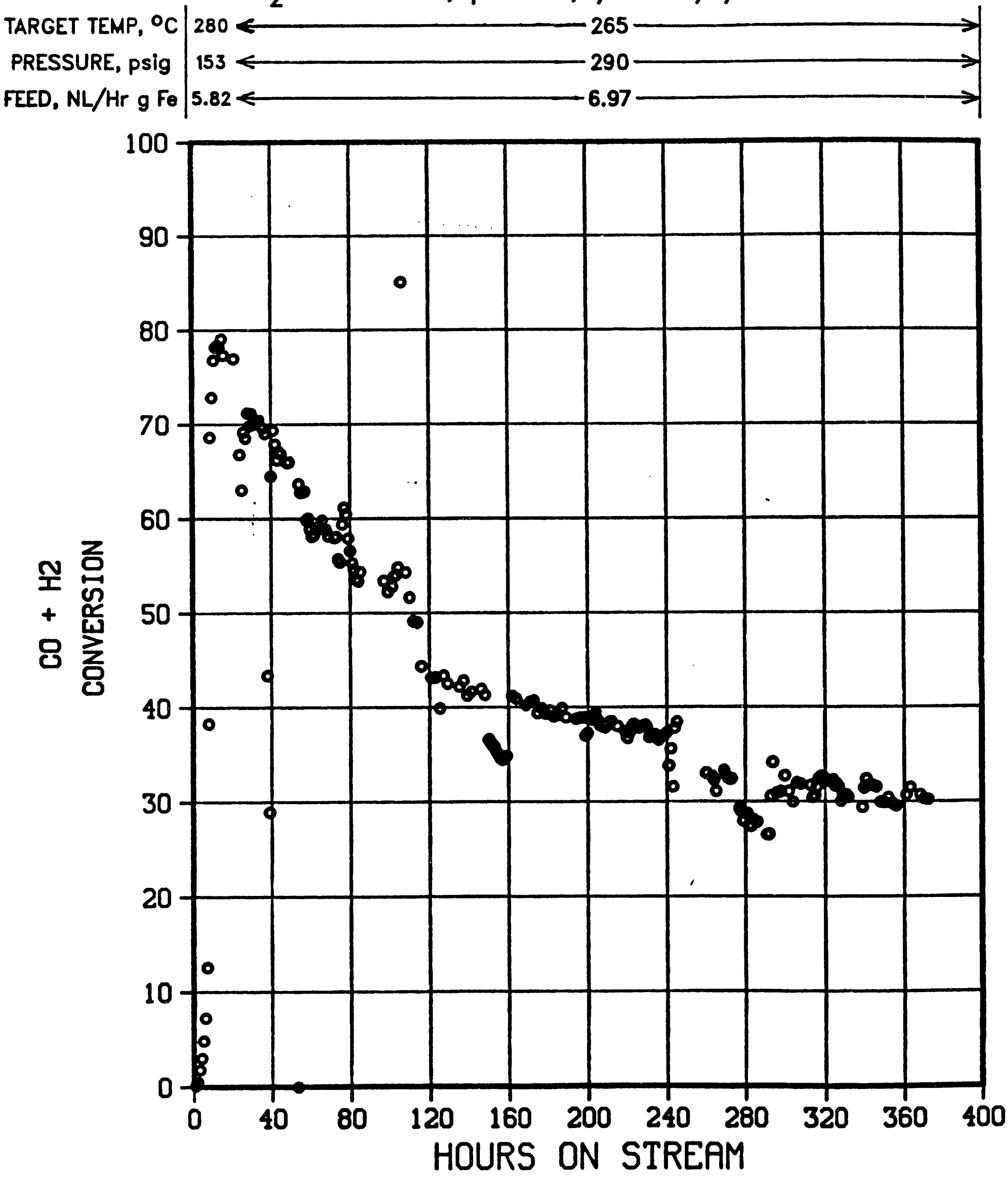


FIGURE A-12

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

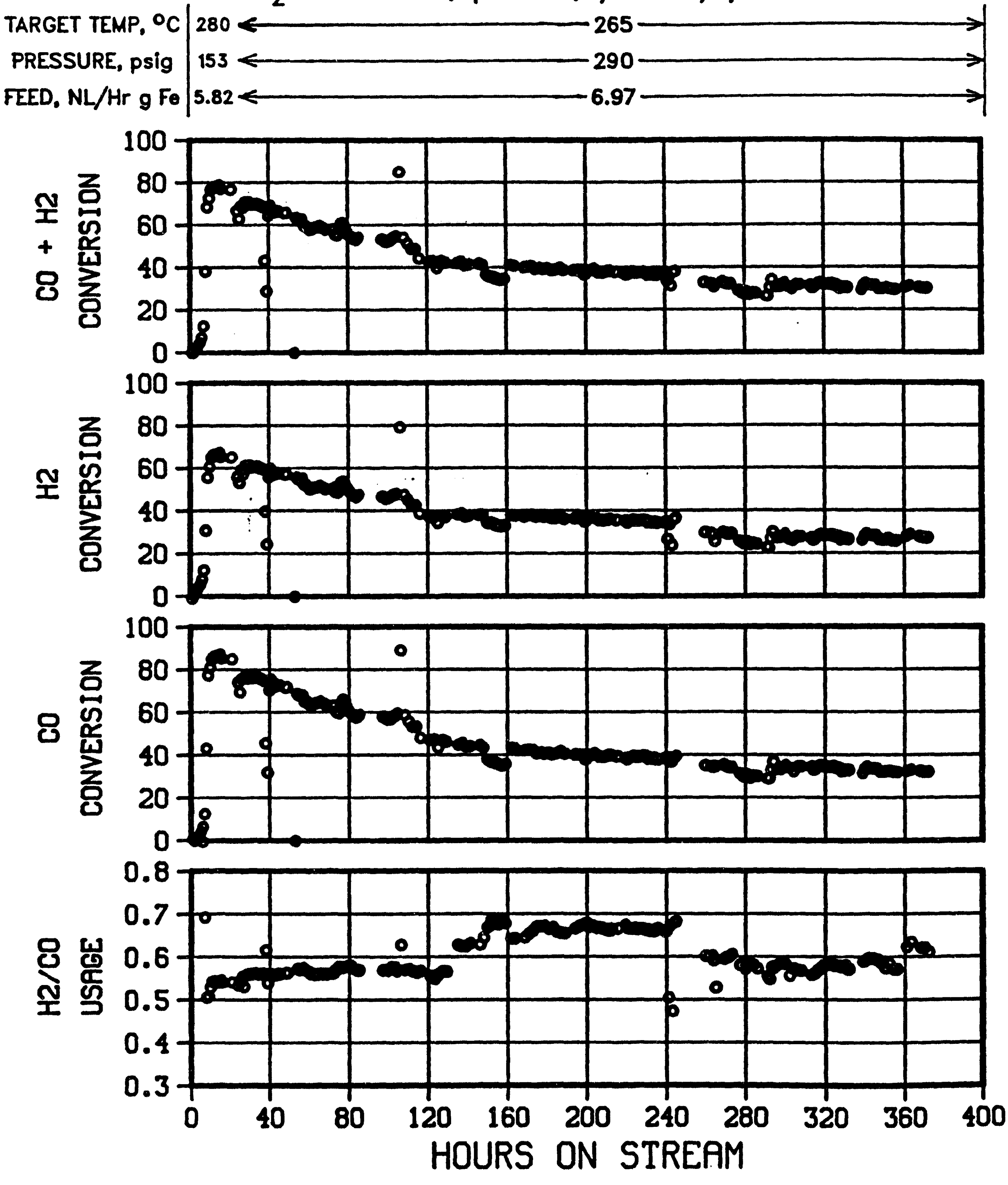


FIGURE A-13

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27-->4/11/93

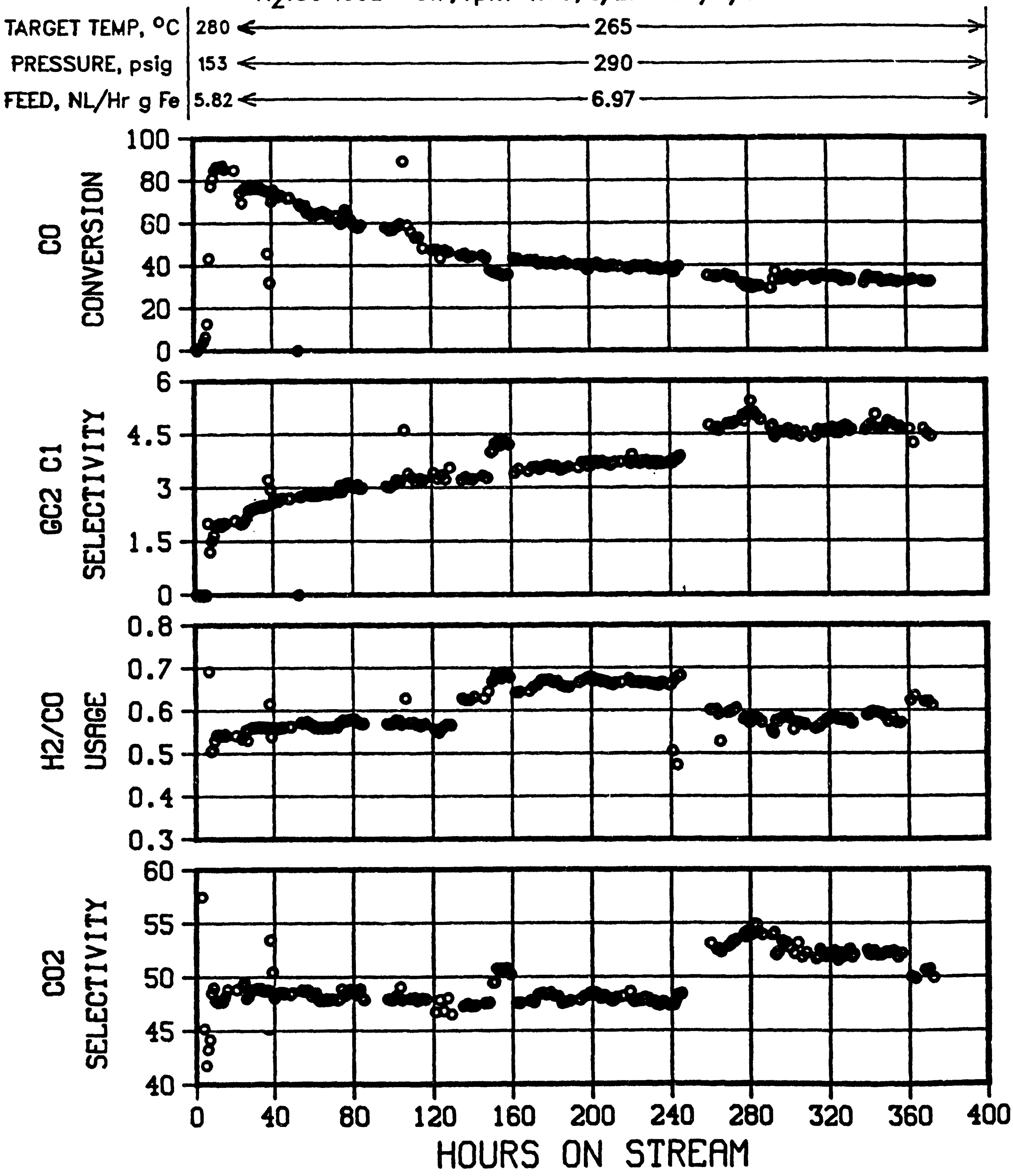


FIGURE A-14

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27––>4/11/93

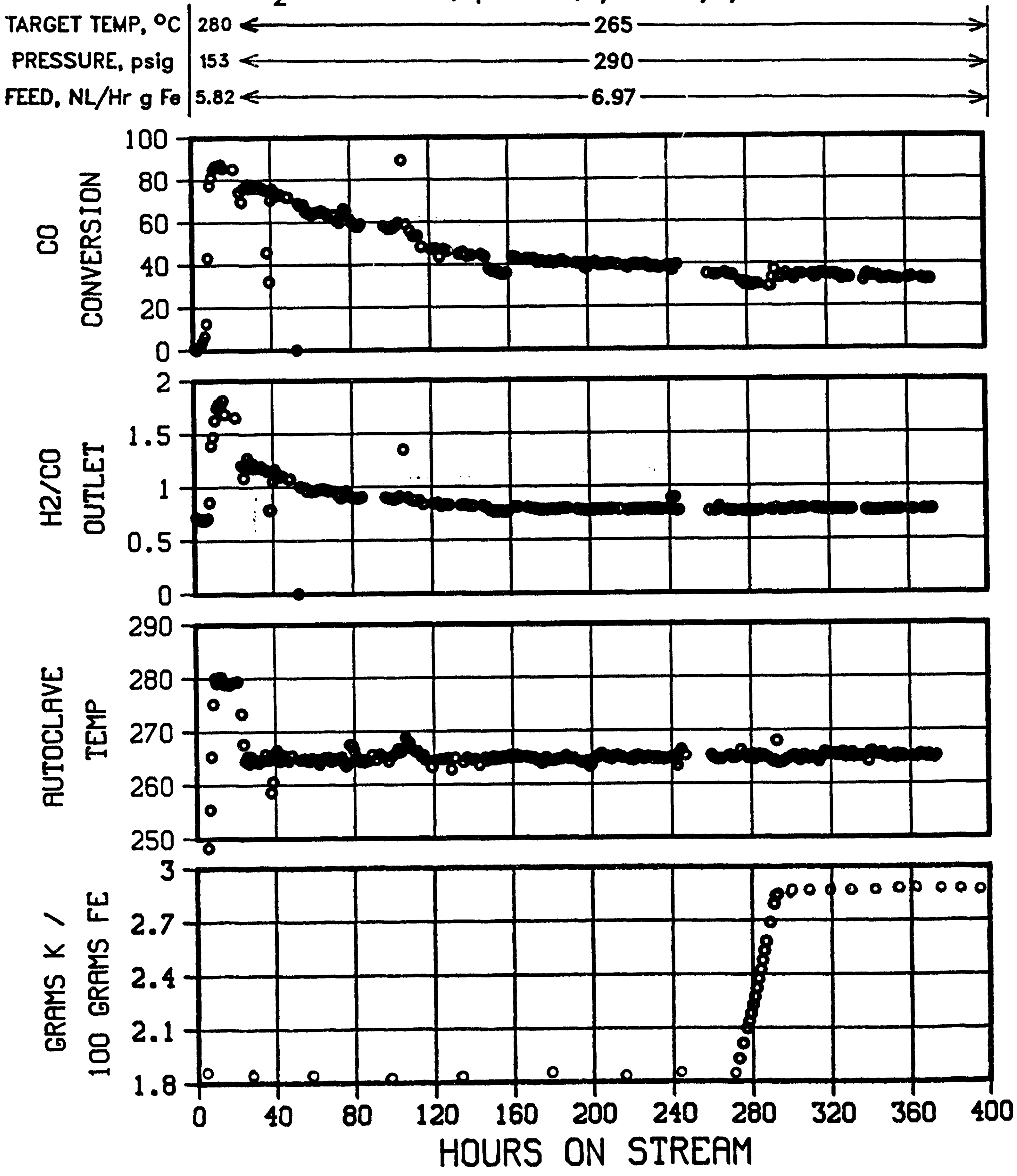


FIGURE A-15

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27––>4/11/93

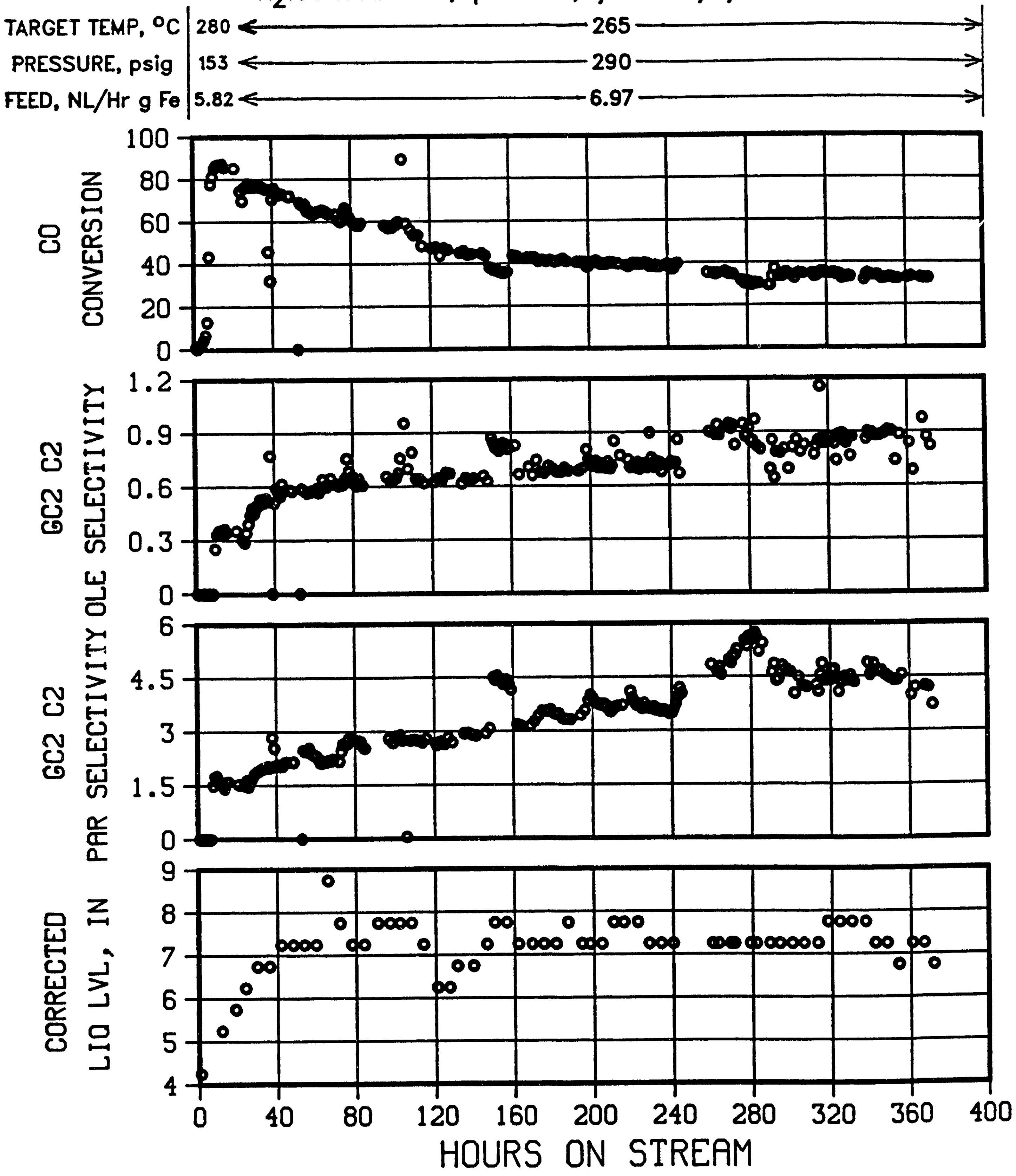


FIGURE A-16

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27––>4/11/93

TARGET TEMP, °C | 280 ← 265 →

PRESSURE, psig | 153 ← 290 →

FEED, NL/Hr g Fe | 5.82 ← 6.97 →

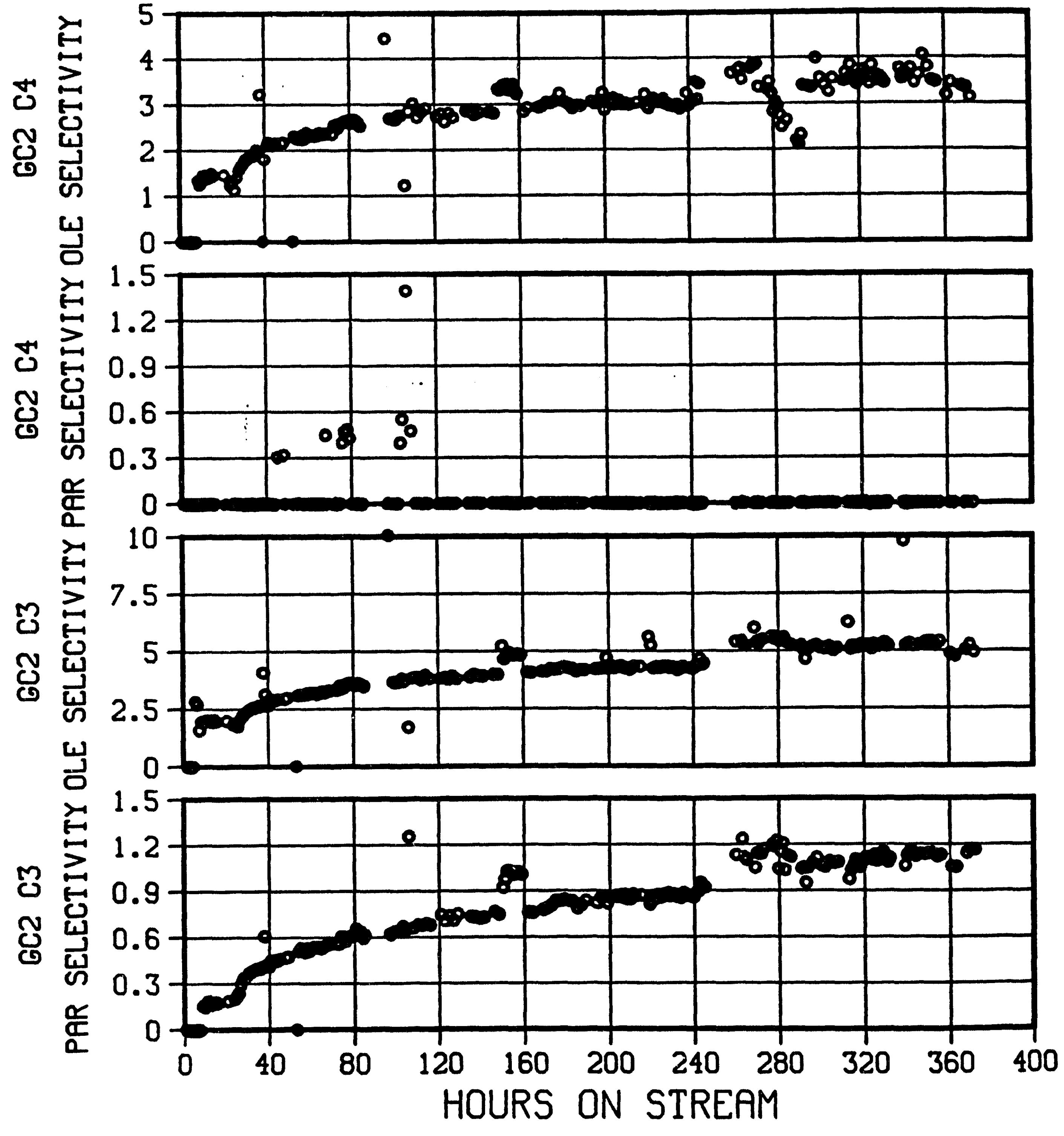
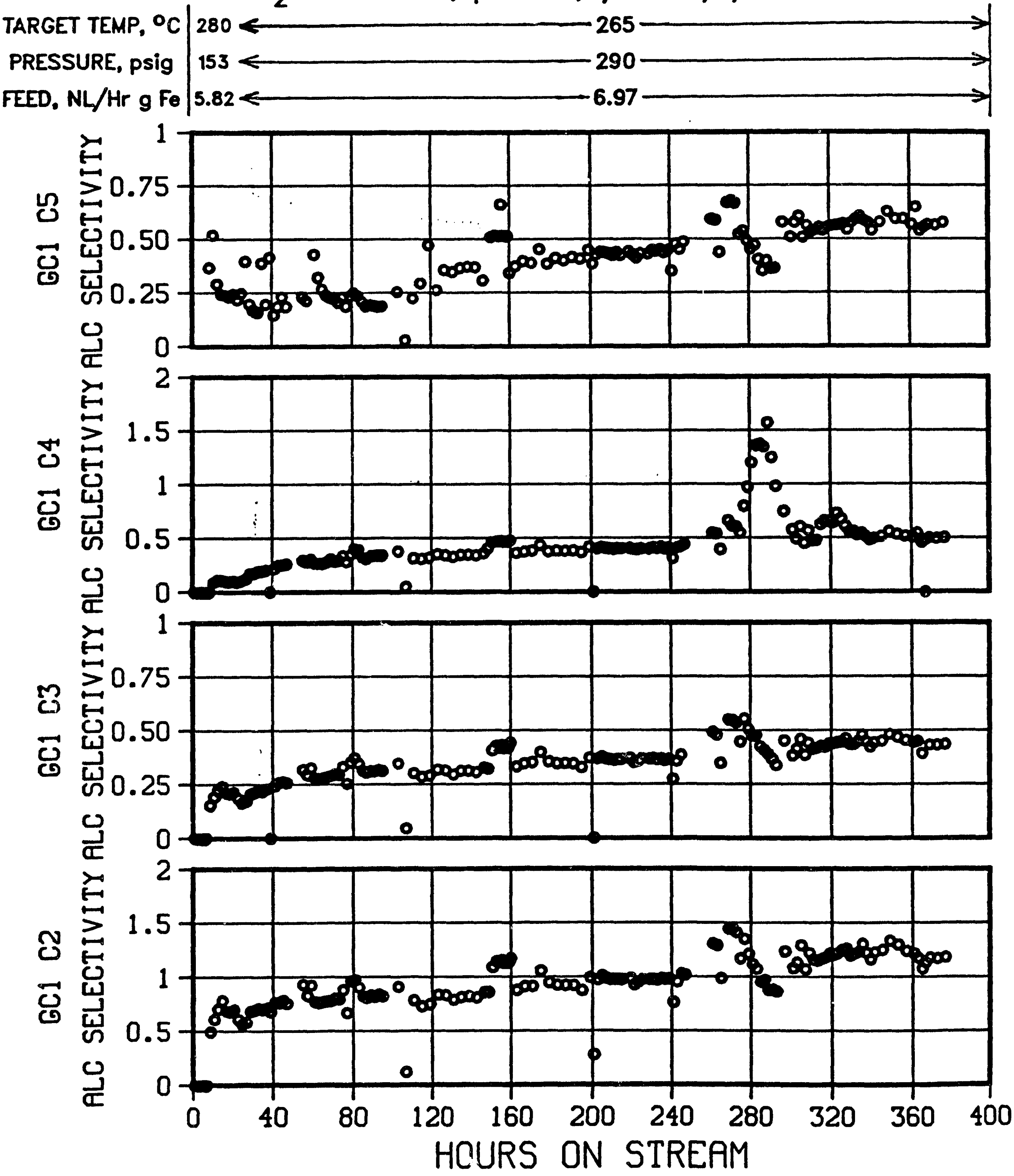


FIGURE A-17

PRECIPITATED IRON CATALYST IN SLURRY AUTOCLAVE REACTOR

PLANT 701 R–65 25g 6827–108A in 290g C_{30} oil

H_2:CO feed = 0.7, rpm=1100, 3/27-->4/11/93



DATE
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5/31/94

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