DOE/PC/79812-T6

The Development of Precipitated Iron Catalysts with Improved Stability

Contract DE-AC22-87PC79812

DOE/PC/79812--T6

DE92 014629

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Technical Progress Report No. 9
(9/16/89-12/16/89)

Contract Objective

The objective of this program is to identify the chemical principles governing the deactivation of precipitated iron catalysts during Fischer-Tropsch synthesis and to use these chemical principles in the design of catalysts suitable for slurry reactors. The performance targets are 88% $CO+H_2$ conversion with less than 1% deactivation/day for 1 month and a methane and ethane selectivity of no more than 7% (based on hydrocarbons and oxygenates only) at a space velocity of at least 2 normal liters per hr per gram iron (NL/hr/gFe) using a synthesis gas with 0.5-1.0 H_2:CO ratio in a slurry reactor.

Contract Tasks

Task 1.0: Develop an integrated pilot plant

Task 2.0: Evaluate a reference iron catalyst

Task 3.0: Develop a baseline iron catalyst

Task 4.0: Elucidate the deactivation chemistry for iron catalysts

Task 5.0: Investigate catalyst chemistry approaches for improved stability

Task 6.0: Write final report

Scope of the Work

Previous work under this contract involved the following:

DISCLAIMER

9/16/87-3/16/88

Task 3.0: four catalysts were prepared by precipitation at different pH levels and were characterized.

3/16/88-6/16/88

Task 1.0: the design work necessary for upgrading the existing fixed-bed pilot plant with slurry and Berty reactor testing capabilities was completed.

6/16/88-9/16/88

Task 3.0: a catalyst preparation plant was designed and constructed.

9/16/88-12/16/88

Task 2.0: experiments determined that the fused iron ammonia synthesis catalyst C-73-1-101 cannot be properly activated in situ in the fixed-bed pilot plant at the relatively low temperatures of 200-300°C, that are typical of the Fischer-Tropsch process.

Task 3.0: an experimental iron catalyst tested in the fixed-bed pilot plant was shown to have acceptable stability and higher than desired methane and ethane selectivity.

12/16/88-3/16/89

Task 2.0: the MCSG-4 catalyst from Mobil was shown to have unexpectedly low activity in the fixed-bed reactor test.

3/16/89-6/16/89

Task 3.0: the construction of the slurry autoclave pilot plant was completed, and an experimental iron catalyst was used for plant shakedown.

6/16/89-9/16/89

Task 3.C: the filter assembly in the autoclave reactor was modified, and an experimental iron catalyst was tested with the new configuration. The ceramic filter with 0.15 μm pore size plugged during the test.

During this reporting period (9/16/89-12/16/89), filters with larger pore sizes were used in the slurry autoclave reactor. An experimental iron catalyst was tested four times under Task 3.0.

Experimental

The slurry-bed pilot plant was previously described in the technical progress report covering the period of 3/16/88-6/16/88. The filter assembly, stirring procedure, and the feed system were described in the technical progress report covering the period of 6/16/89-9/16/89. Four runs (Runs 6-9) were conducted during this reporting period (9/16/89-12/16/89). The iron catalyst identification, the nature of initial wax medium, the catalyst and initial wax weights, the height of the static slurry, and the location and the pore size of the filter are summarized in Table 1. The catalyst and the C_{32} paraffin wax medium were loaded into the 1-liter-autoclave reactor at 120°C. The 4-liter-autoclave was not used for this work. The 1-liter-autoclave was pressure tested with N_2 at 120°C and 18 atm. After a successful pressure test, the pressure was lowered to 11 atm, and the temperature was increased to 280°C under N_2 flow.

Synthesis gas with 0.7 H_2 : 1 CO feed ratio was introduced at 280°C. During the first 12 hr, the catalyst was activated at 280°C and 11 atm using a space velocity of 1.7-2.0 NL/hr/gFe. Conditions were changed between 12 and 15 hr on-stream. After 15 hr, the temperature was set at 258°C, the pressure at 15 atm and the space velocity at 1.2-1.4 NL/hr/gFe. Autoclave internal temperatures, pressures, feed compositions, feed rates, space velocities, and stirrer speeds in revolutions/minute (rpm) at different hours on-stream are also summarized in Table 1.

Argon was present in the synthesis gas feed at about 6% (by mole) level and was used as an internal standard for determining conversions and light hydrocarbon selectivities according to the following expressions:

$$\text{CO Conversion, \%} = (((CO/Ar)_{feed}-(CO/Ar)_{product})/(CO/Ar)_{feed}) * 100$$

The CO + H_2 conversion was calculated in a similar manner. The calculation for carbon atom selectivity to CO_2 was:

$$((CO_2/Ar)_{product}/((CO/Ar)_{feed}-(CO/Ar)_{product})) * 100$$

The carbon atom selectivity to a hydrocarbon with n carbons, C_n, was:

$$((C_n/Ar)_{product} * n/((CO/Ar)_{feed}-(CO/Ar)_{product})) * (100/(100-CO_2 \text{ Selectivity})) * 100$$

The hydrocarbon and oxygenate carbon atom selectivities were normalized to a total of 100% to back out CO converted to CO_2. The H_2:CO usage ratio was:

(H_2 conversion/CO conversion)*(H_2:CO feed ratio).

Results and Discussion

The catalytic performances in Runs 6-9 are summarized in Figures 1-20.

In Run 6, a ceramic filter, which had a nominal pore size of 0.7 μm, was used. The bottom of the filter was 1.19 in. above the static liquid level in the autoclave. In Run 6, like in all other runs, the objective was to maintain the liquid level in the autoclave by continuously withdrawing the liquid products made. Liquid products were withdrawn by maintaining a pressure differential across the filter. The product gas also exited the autoclave through the filter. The outlet of the filter was connected to the high temperature, high pressure product collector. Following activation, a stable $CO+H_2$ conversion of about 78% was obtained at a space velocity between 1.2 and 1.4 NL/hr/gFe. The methane and ethane selectivity gradually increased with time on-stream, and was about 4% at 72 hr. The ceramic filter plugged during the run, as was apparent from the pressure drop across the filter that gradually increased to 16 atm by 72 hr on-stream. The run was shut down at the end of 72 hours.

In Run 7, a metallic filter with a nominal pore diameter of 17 μm and an absolute pore diameter of 45 μm was used to prevent the filter from plugging with catalyst particles. The bottom of the filter was initially immersed 1/8 in. in the static slurry. The filter did not plug during the run, but the products collected through the filter contained a lot of catalyst. Following activation, the $CO+H_2$ conversion gradually decreased to about 15% by 75 hr on-stream. The decline of the conversion probably resulted from the loss of catalyst across the filter. The selectivity to methane decreased during the run, which suggests that the methane selectivity is lower at low conversions.

In Run 8, the filter had a nominal pore size of 5 μm and an absolute pore size of 18 μm. The bottom of the filter was 1/4 in. above the static slurry level.

The filter did not plug during the run, but the products that were collected through the filter still contained a lot of catalyst. Because the initial catalyst particle size was 37-105 μm, significant catalyst attrition must have occurred during the run. A gradual decline in conversion was again observed, probably because of the catalyst loss.

Run 9 used the same type of filter that was used in Run 8, and similar results were obtained.

Summary

The 0.7 μm ceramic filter that was used for withdrawing the liquid products from the autoclave reactor rapidly plugged with catalyst particles. Plugging did not occur, but substantial amount of catalyst was lost when larger pore size filters (5 or 17 μm nominal pore diameter) were used. Data indicate that iron catalysts undergo significant attrition during tests in the slurry autoclave reactor.

Table 1
Run Information

Run	Plant	Catalyst							Wax Medium			Rpm	Temp. In °C	Filter		Pres Out, atm	Feed						Hours
		Number	% Fe			Wt., g	Mesh Size	Static Hgt, In.	Nature	% Solids	Wt, g (wax)			Pore Size, μ	Height Inches		% H_2	% CO	% Ar	H_2:CO	Rate scc/min	NL/hr /gFe	
6	700B	5709-139	64.0			107.5	140-400	4 11/16	C_{32}	22	380	1000	280	0.7	5 ⅛	11	39.17	55.19	5.64	0.71	2270	2.0	0-12
													258			15							12-15
																					1600	1.4	15-33
																	38.90	55.03	6.07	0.71	1600		33-56
																	39.57	54.60	5.83	0.73			56-72

Table 1
Run Information

Run	Plant	Catalyst							Diluent			Rpm	Temp, In, °C	Filter		Press Out, atm	Feed						Hours
		Number	% Fe			Wt, g	Mesh Size	Static Ht, in	Nature	% Solids	Wt, g (wax)			Pore Size, μ	Height Inches		% H_2	% CO	% Ar	H_2:CO	Rate scc/min	NL/h /gFe	
7	700B	5709-139	64			107.5	140-400	4 ½	C_{32}	22	380	1000	280	17-45	4 ⅝	11	39.49	54.56	5.95	0.72	1980	1.7	0-12
												↓	↓			↓	↓	↓	↓	↓	1420	1.2	12-15
												↓	258			15	↓	↓	↓	↓	↓	↓	15-27
												1250	↓			↓	↓	↓	↓	↓	↓	↓	27-34
												↓	↓			↓	39.49	54.68	5.83	0.72	↓	↓	34-51
												1000	↓			↓	↓	↓	↓	↓	↓	↓	51-75
												↓	↓			↓	↓	↓	↓	↓	↓	↓	
8	700B	5709-139	64			95	140-400	4 ⅝	C_{32}	20	380	1000	280	5-18	4 ⅛	11	39.64	54.41	5.95	0.73	1980	2.0	0-12
												↓	265			↓	↓	↓	↓	↓	1420	1.4	12-14
												1200	258			15	↓	↓	↓	↓	↓	↓	14-34
												↓	↓			↓	39.49	54.77	5.74	0.72	↓	↓	34-56
												1300	↓			↓	↓	↓	↓		↓	↓	56-59
												1500	↓			↓	39.57	54.47	5.96	0.73	↓	↓	59-62
												1300	↓			↓	39.57	54.54	5.89	0.73	↓	↓	62-120
												↓	↓			↓	39.27	54.63	6.10	0.72	↓	↓	120-144
												↓	↓			↓	39.49	54.76	5.75	0.72	↓	↓	144-200
												↓	↓			↓	39.49	54.76	5.75	0.72	830	.82	200-208
												↓	↓			↓	39.57	54.55	5.88	0.73	↓	↓	208-216

Table 1
Run Information

Run	Plant	Catalyst							Diluent			Rpm	Temp in °C	Filter		Press Out, atm	Feed						Hours
		Number	% Fe			Wt, g	Mesh Size	Static Ht, in	Nature	% Solids	Wt, g (wax)			Pore Size, μ	Height Inches		% H_2	% CO	% Ar	H_2:CO	Rate scc/min	NL/h /gFe	
9	700B	5709-139	64.0			95	140-400	4 %	C_{32}	20	380	1000	280	5-18	4 15/16	11	39.49	54.77	5.74	0.72	1980	1.9	0-12
												↓	245			↓	39.49	54.62	5.89	0.72	1420	1.4	12-14
												1100	258			15	↓	↓	↓	↓	↓	↓	14-28
												1200	↓			↓	↓	↓	↓	↓	↓	↓	28-30
												1300	↓			↓	39.35	54.77	5.88	↓	↓	↓	30-78

FIGURE 1

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

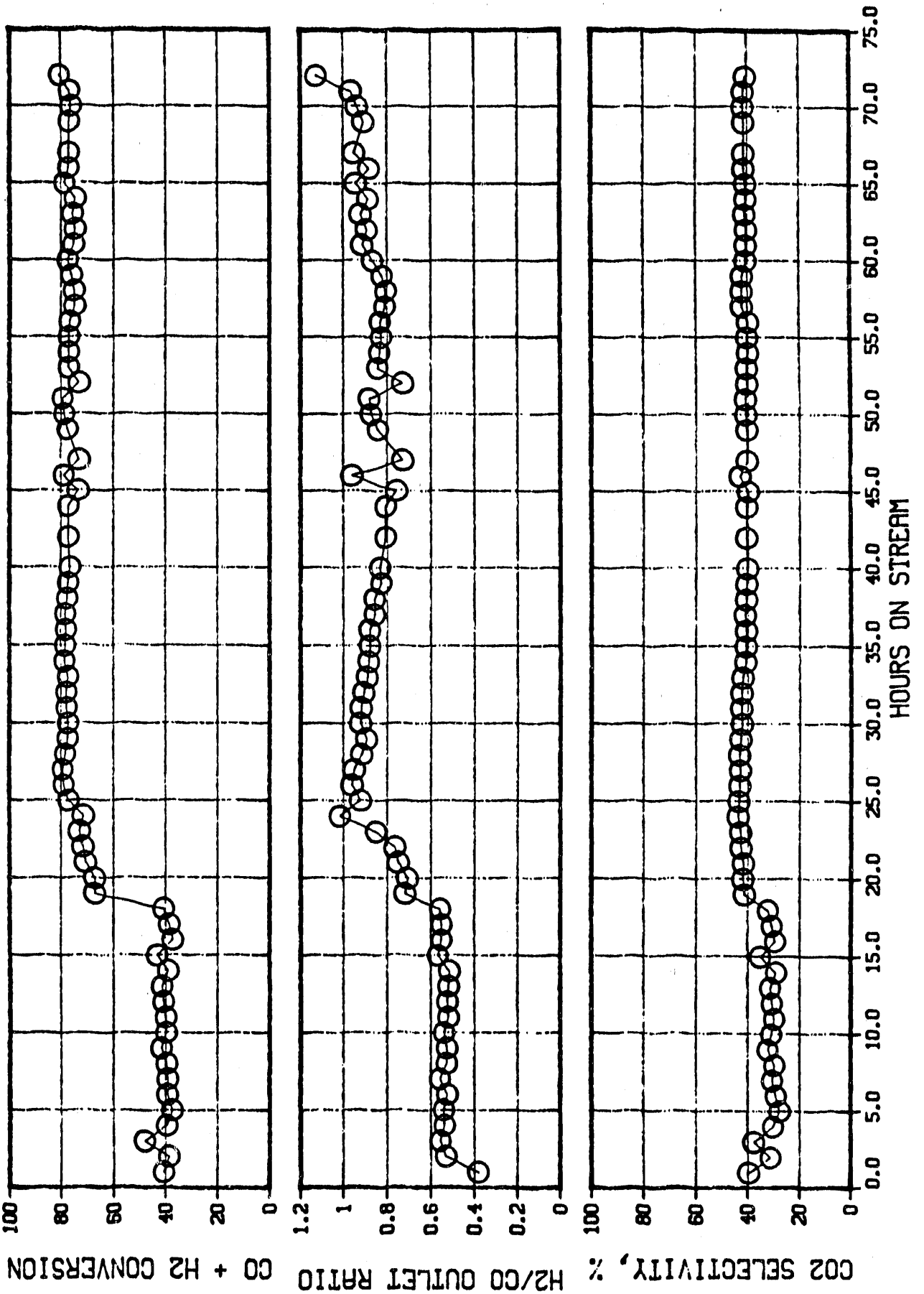


FIGURE 2

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

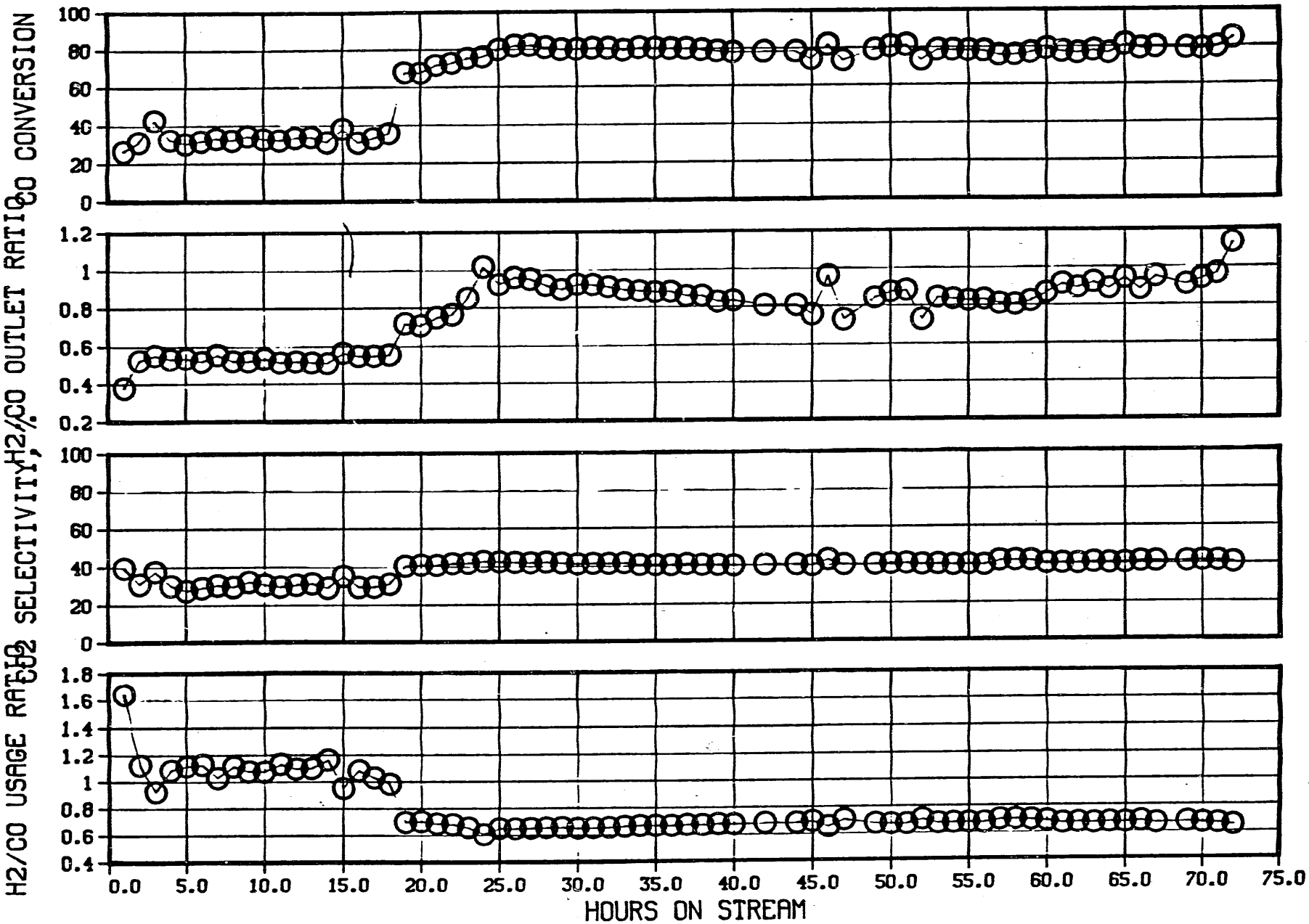


FIGURE 3

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

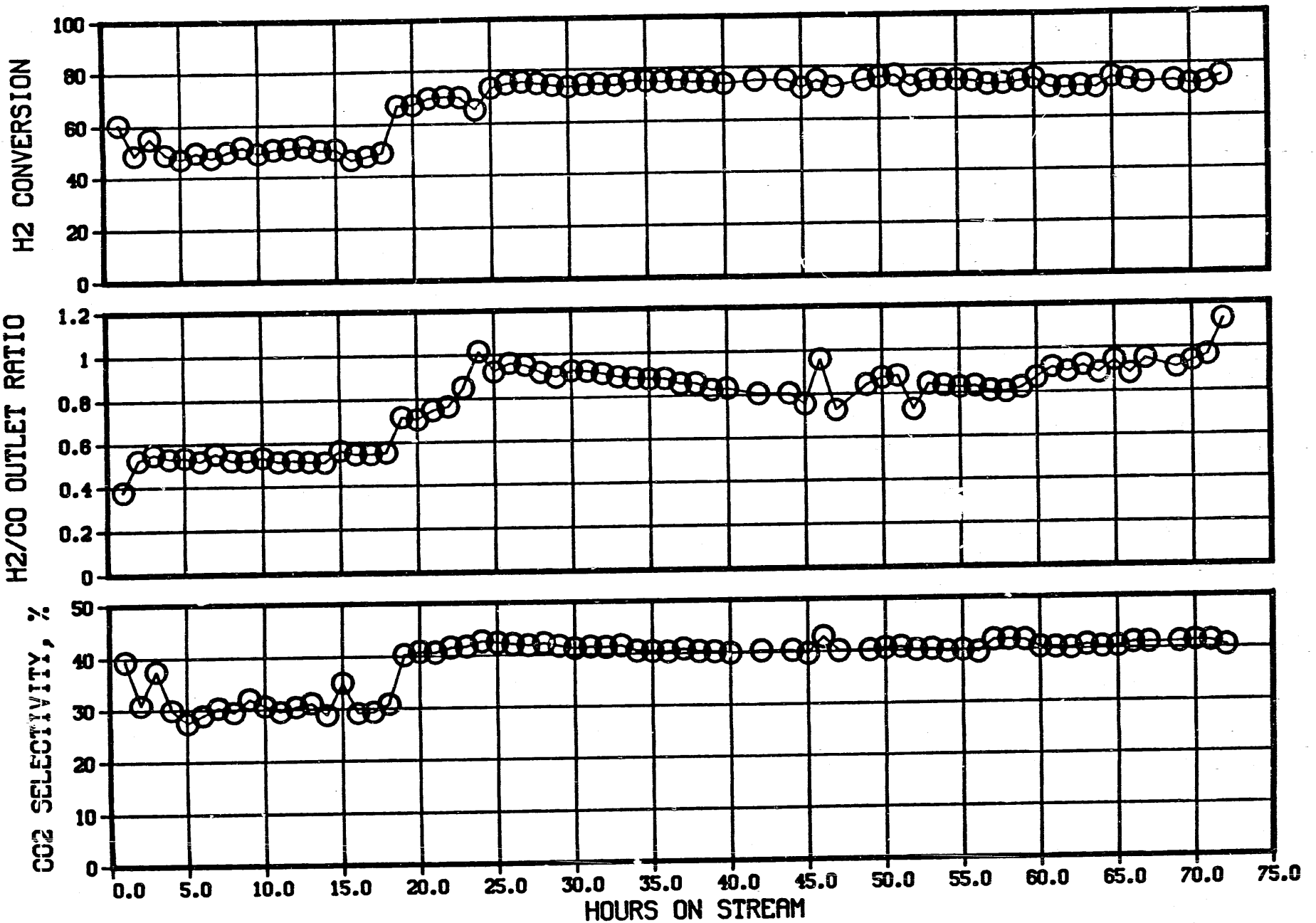


FIGURE 4

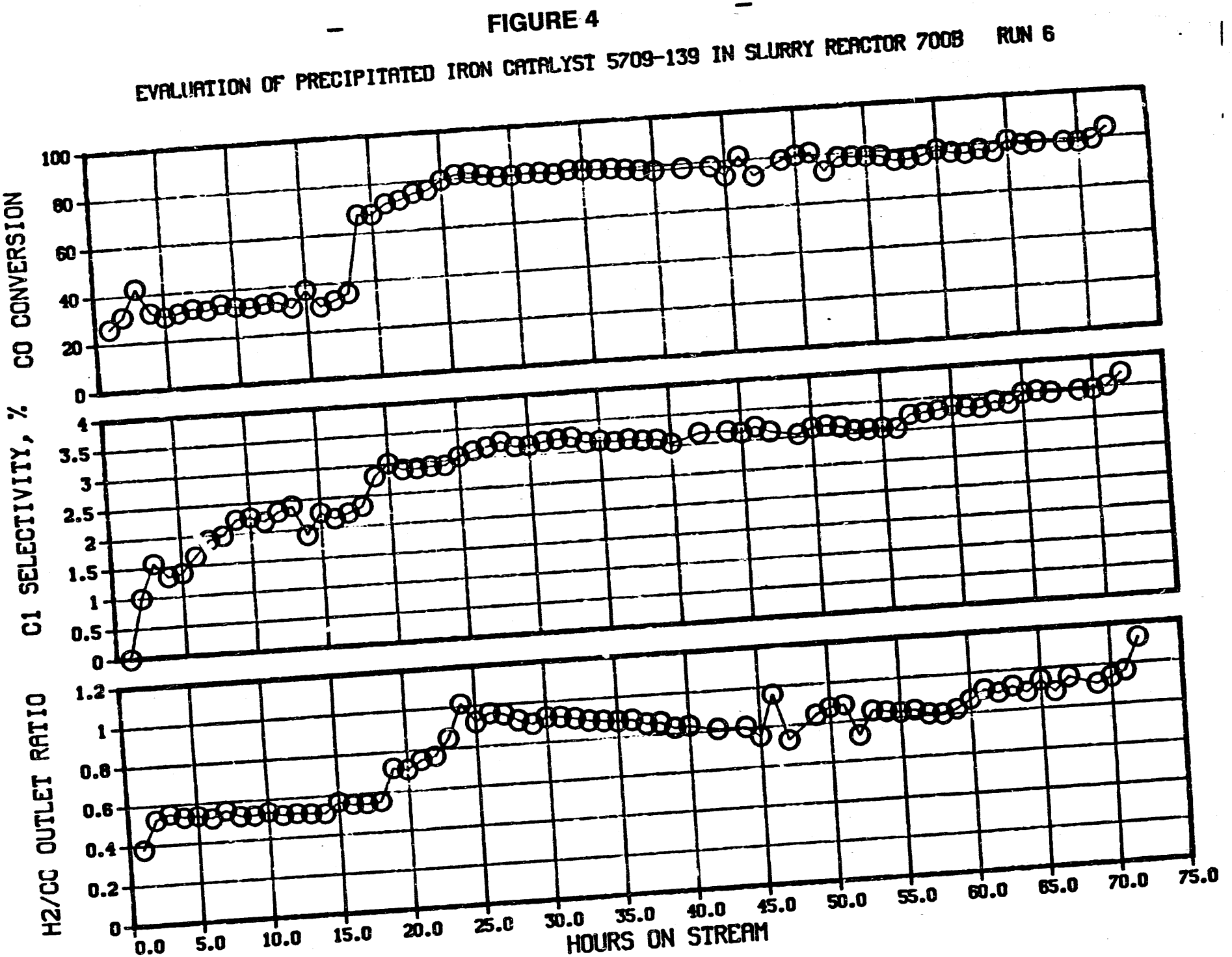

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6
CO CONVERSION
C1 SELECTIVITY, %
H2/CC OUTLET RATIO
HOURS ON STREAM
0
20
40
60
80
100
0.5
1
1.5
2
2.5
3
3.5
4
0.2
0.4
0.6
0.8
1.2
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
75.0

FIGURE 5

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

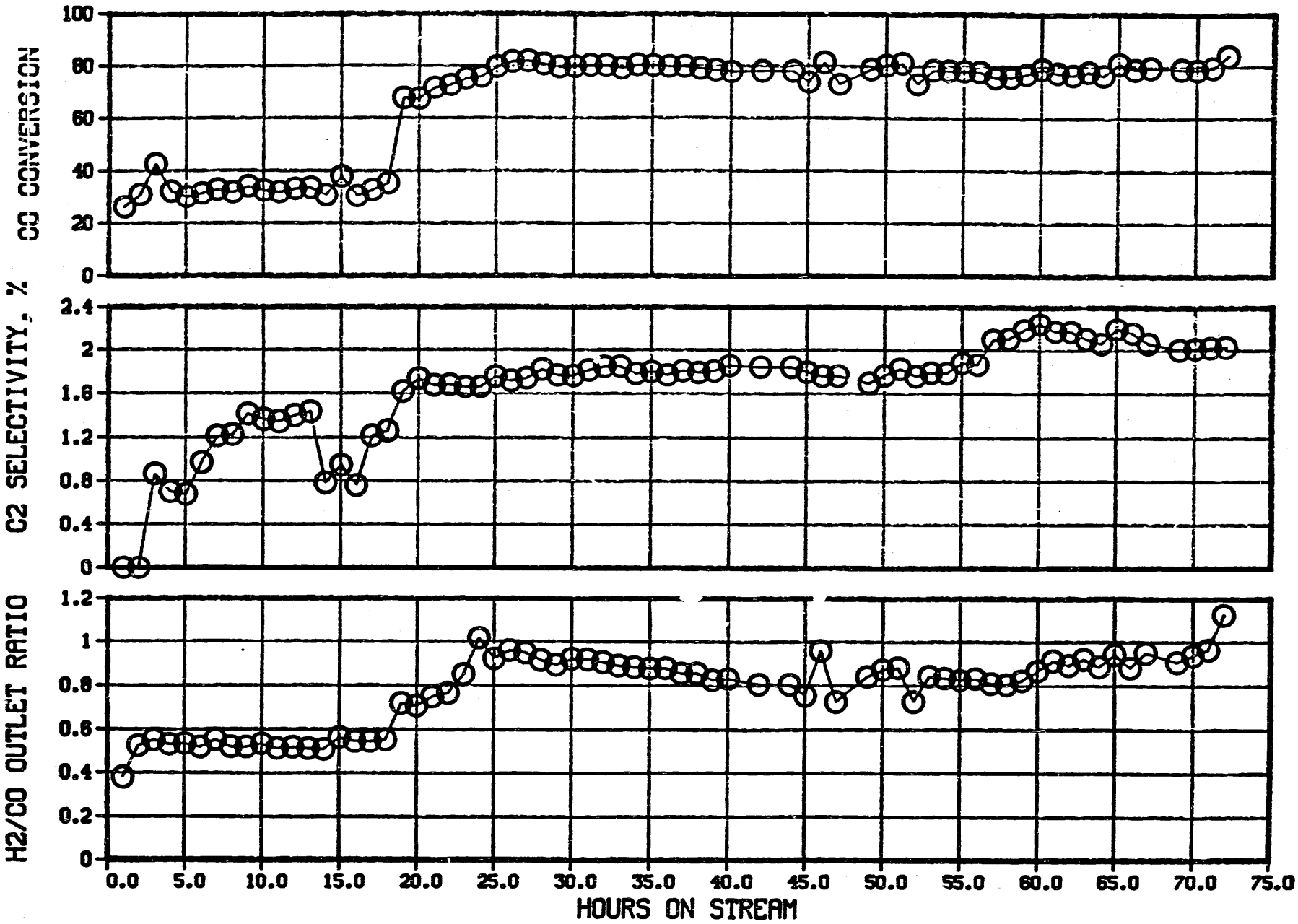


FIGURE 6

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

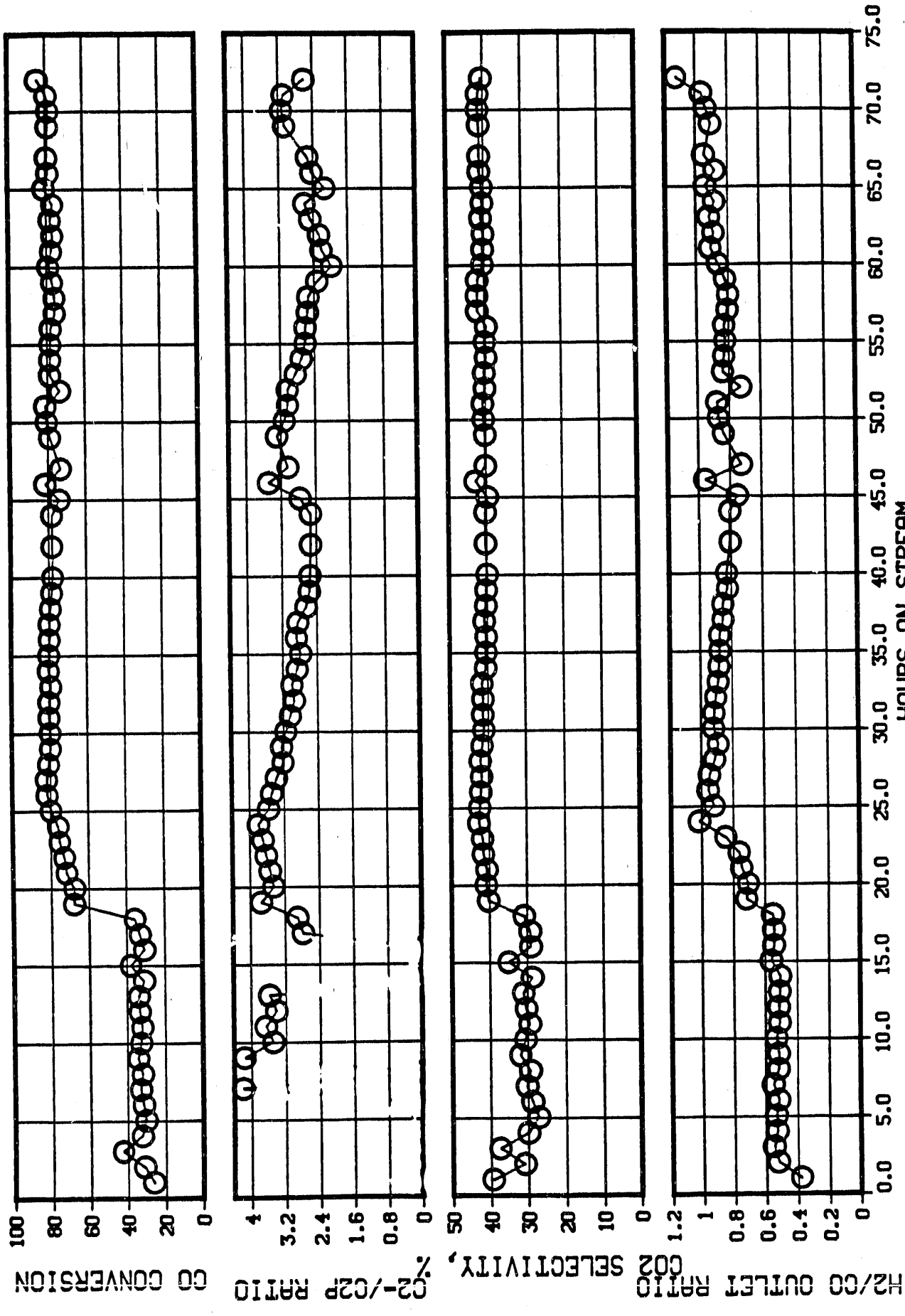


FIGURE 7

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

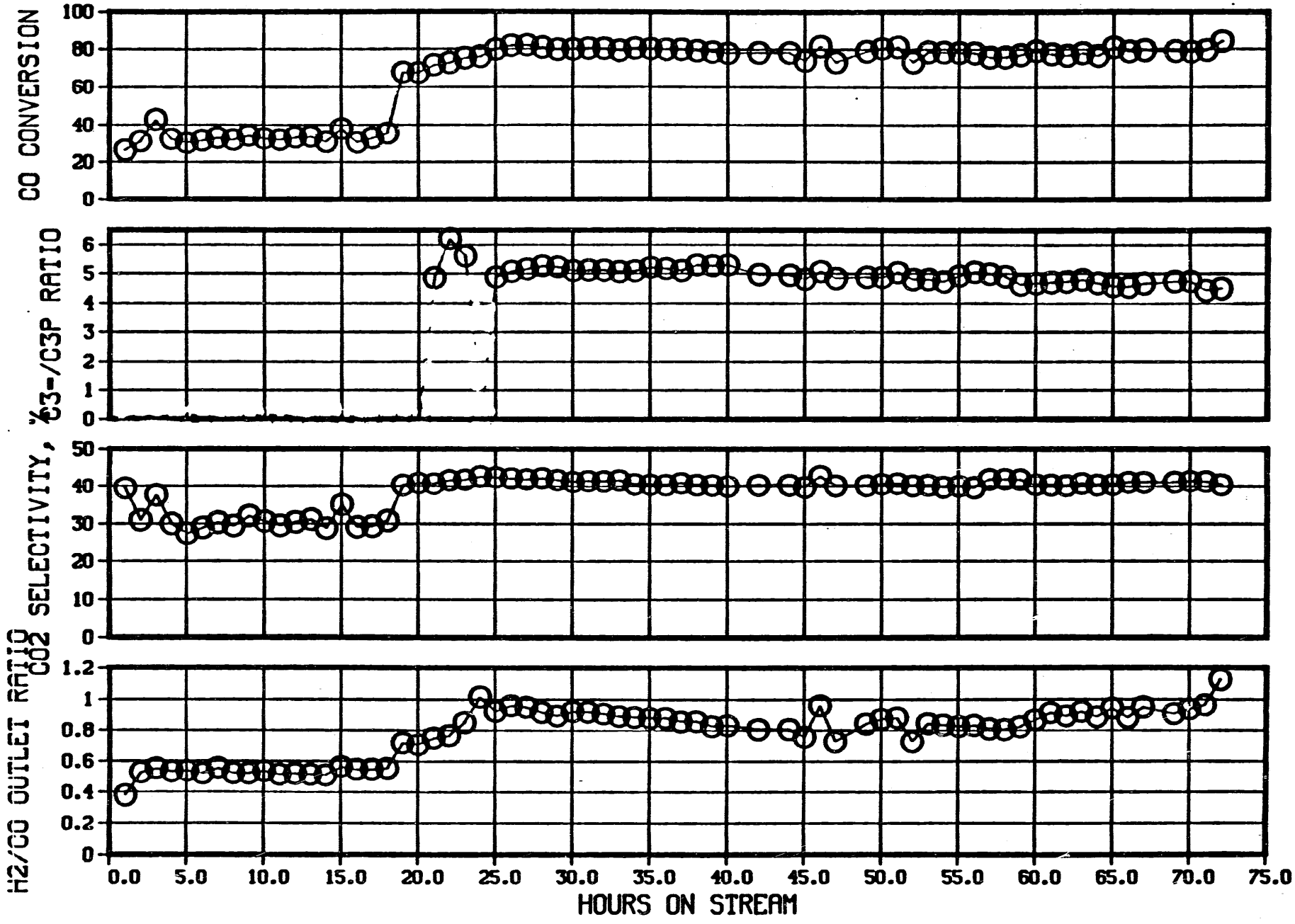


FIGURE 8

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR 700B RUN 6

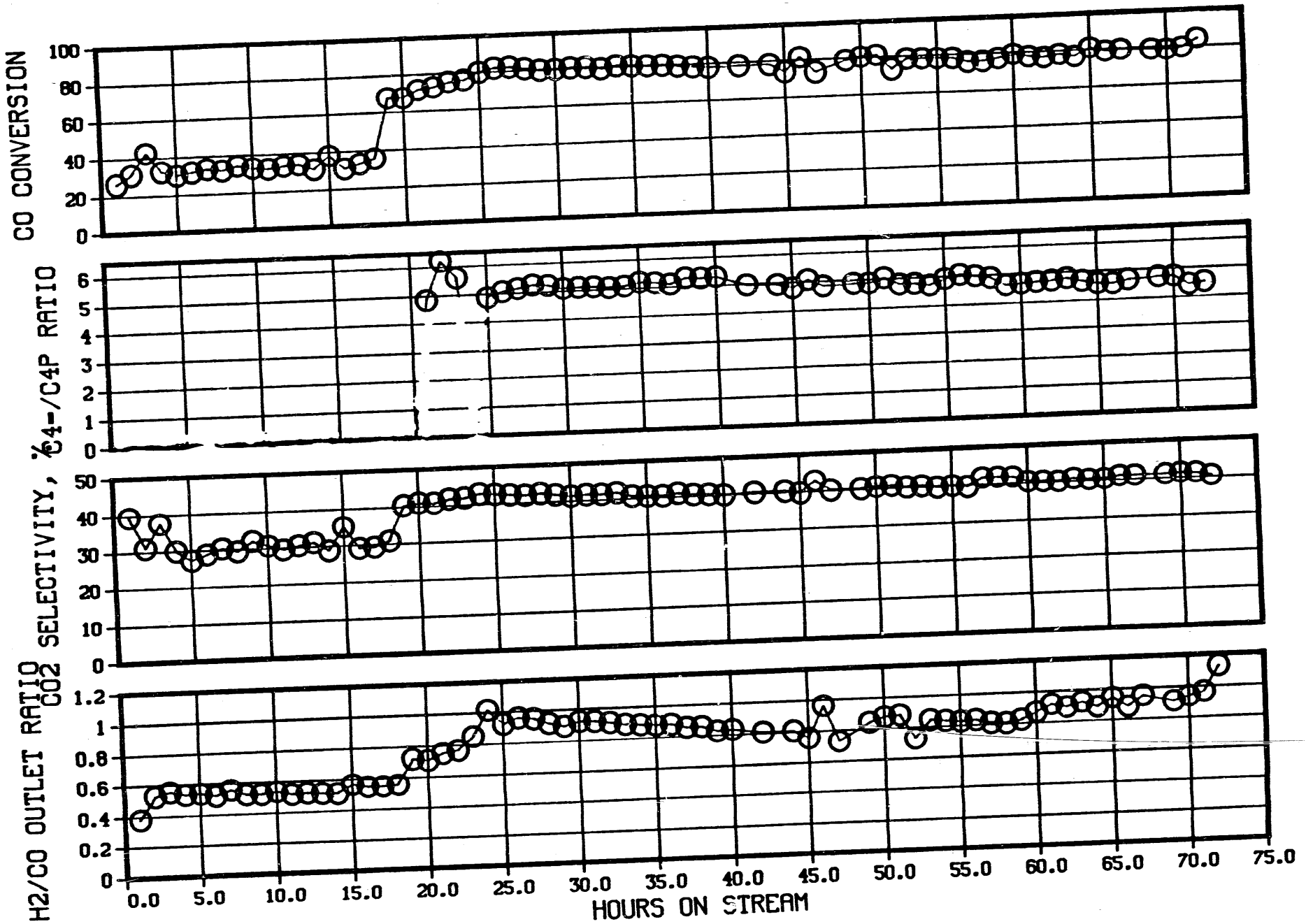


FIGURE 9

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

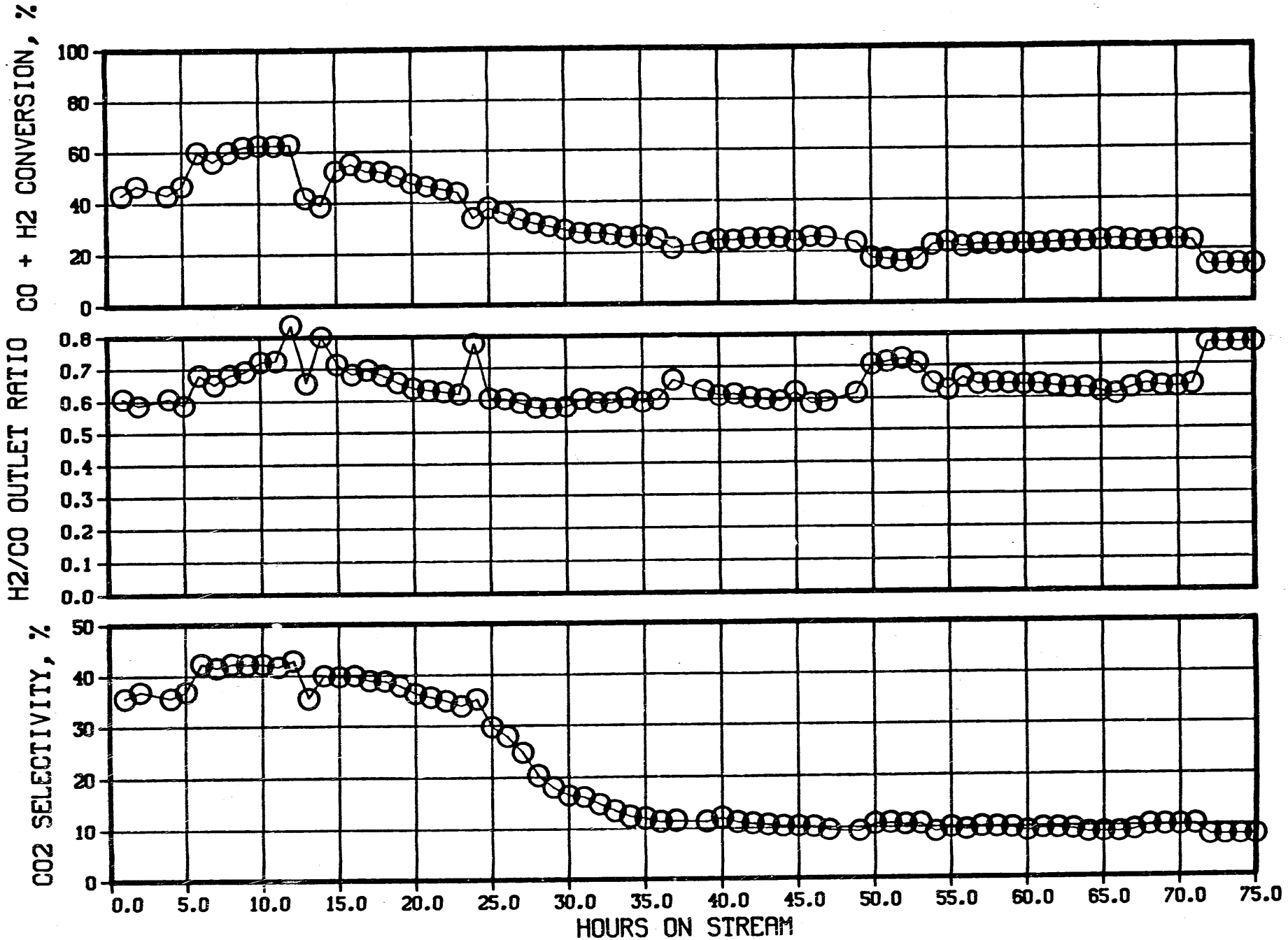


FIGURE 10

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

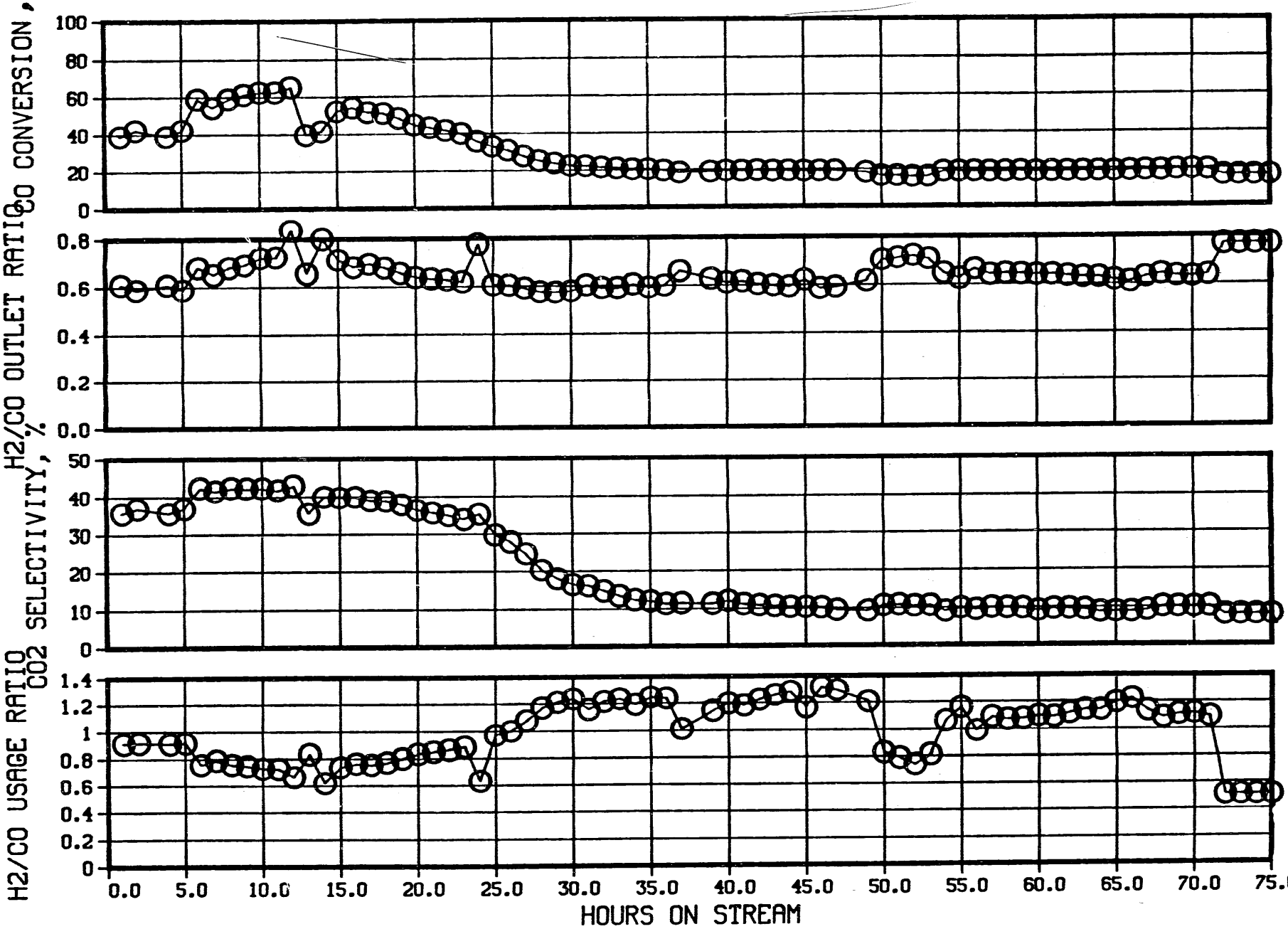


FIGURE 11

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7

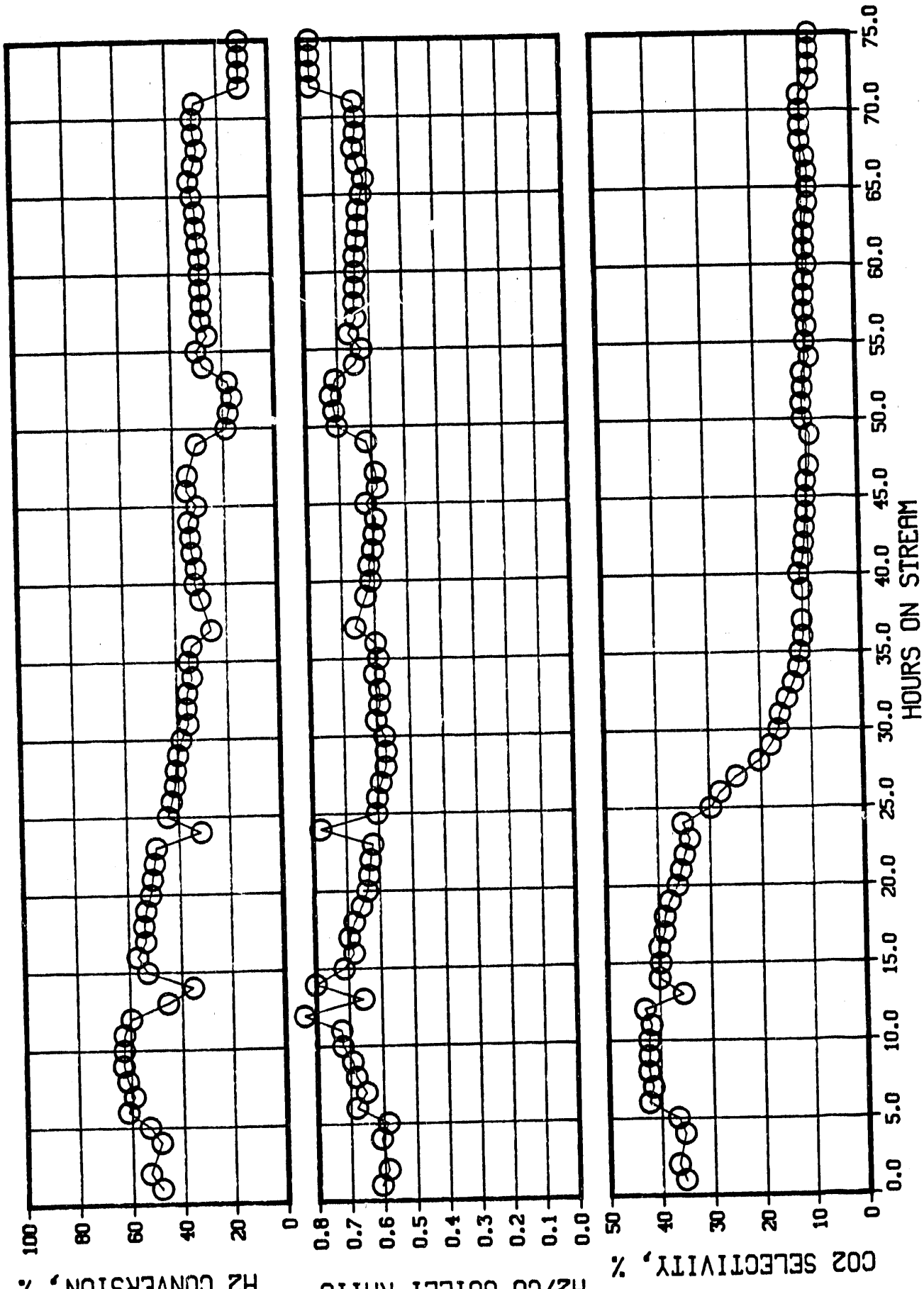
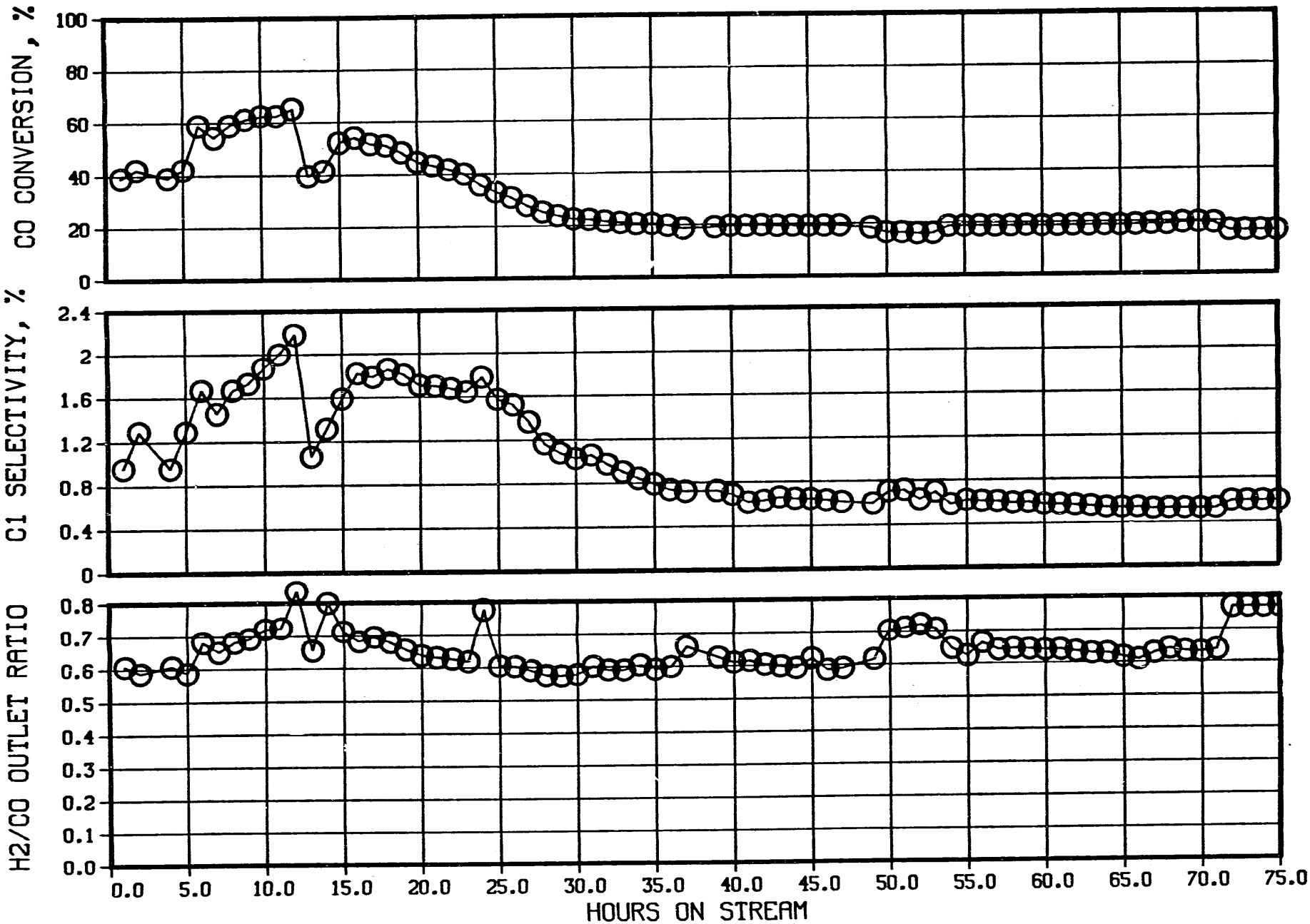


FIGURE 12

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 7



GC2 21

FIGURE 13

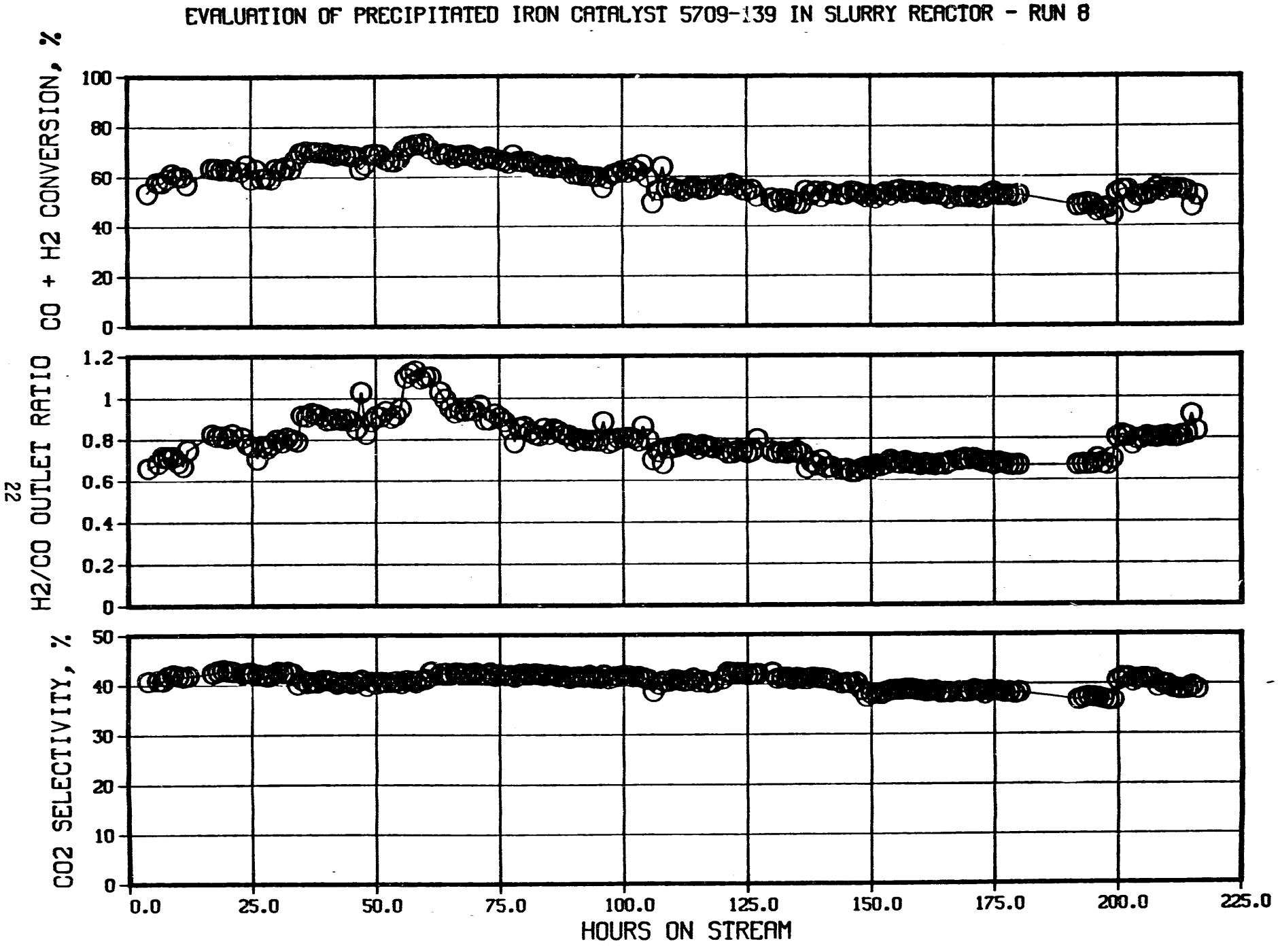

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8
CO + H2 CONVERSION, %
100
80
60
40
20
0
H2/CO OUTLET RATIO
1.2
1
0.8
0.6
0.4
0.2
0
CO2 SELECTIVITY, %
50
40
30
20
10
0
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0
HOURS ON STREAM

FIGURE 14

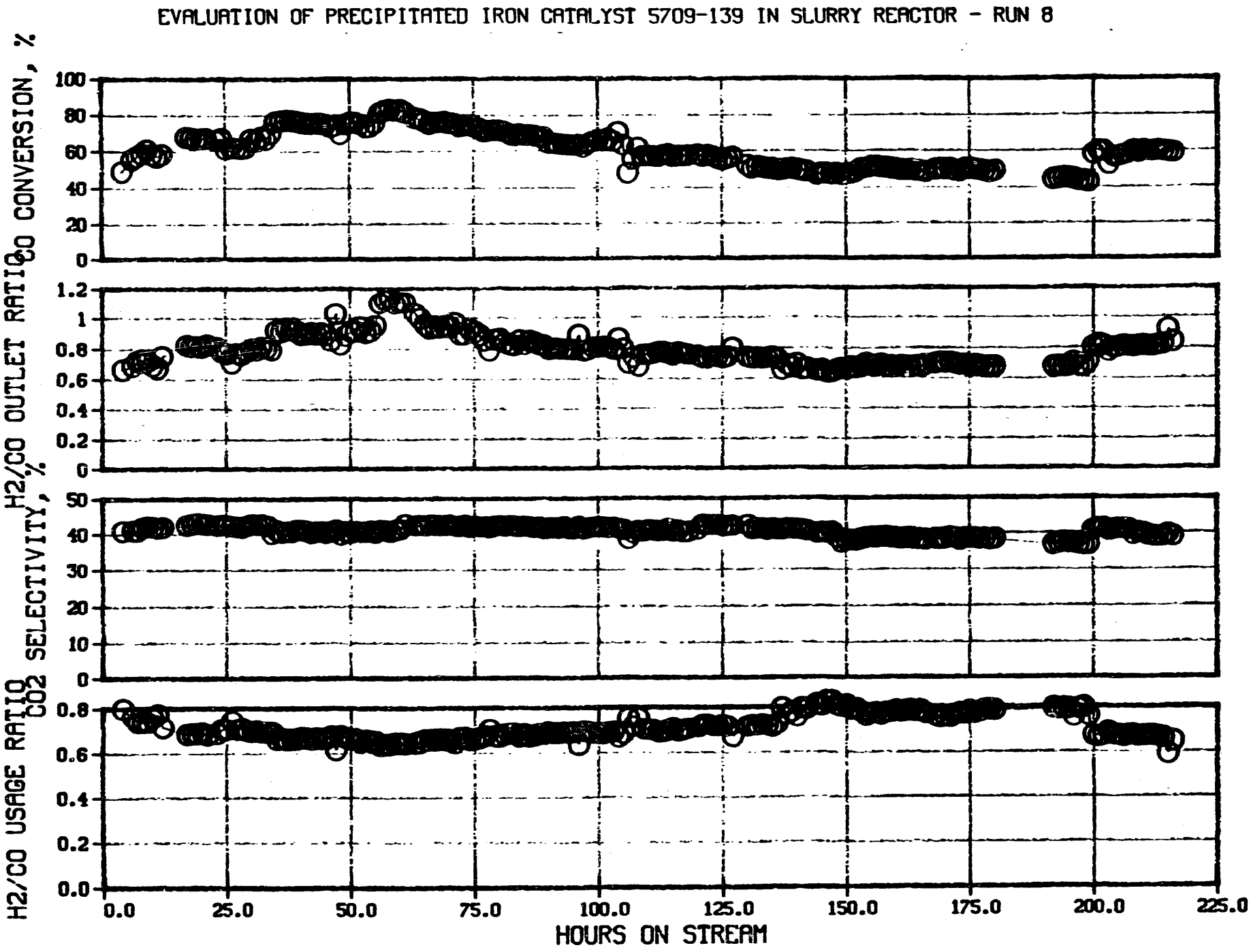

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8
CO CONVERSION, %
H2/CO OUTLET RATIO
CO2 SELECTIVITY, %
H2/CO USAGE RATIO
HOURS ON STREAM
0.0
25.0
50.0
75.0
100.0
125.0
150.0
175.0
200.0
225.0

FIGURE 15

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8

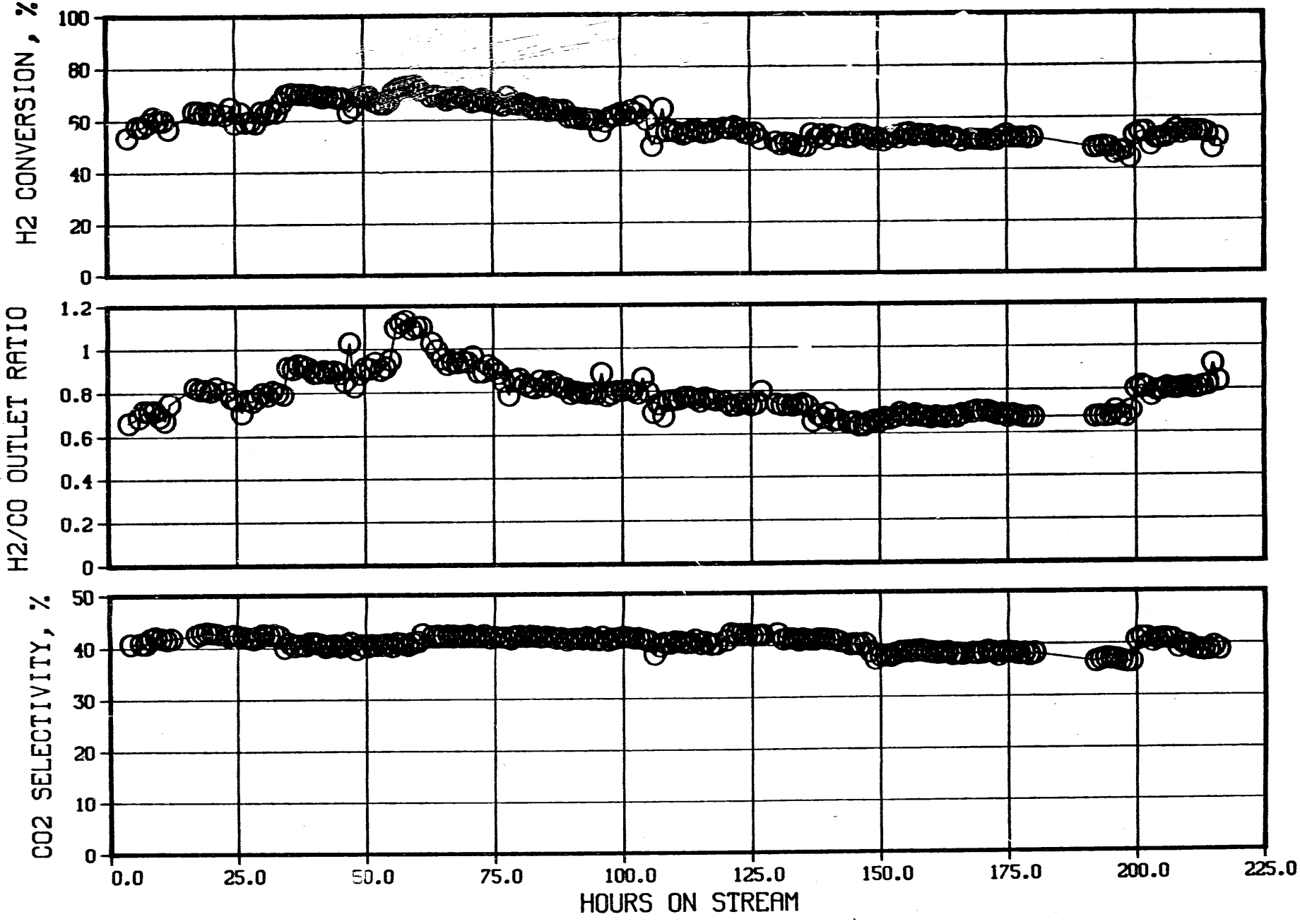
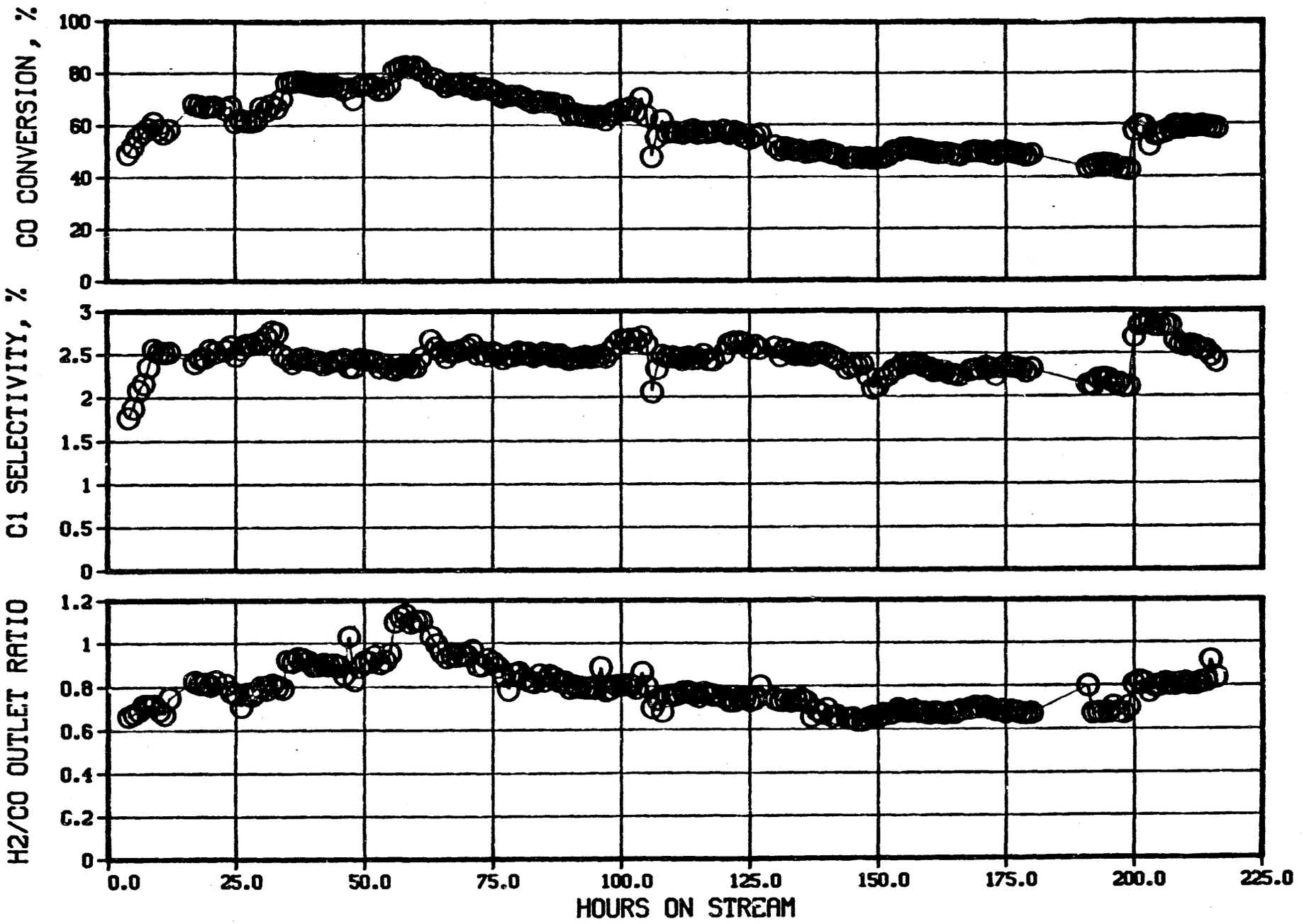


FIGURE 16

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 8



GC2

FIGURE 17

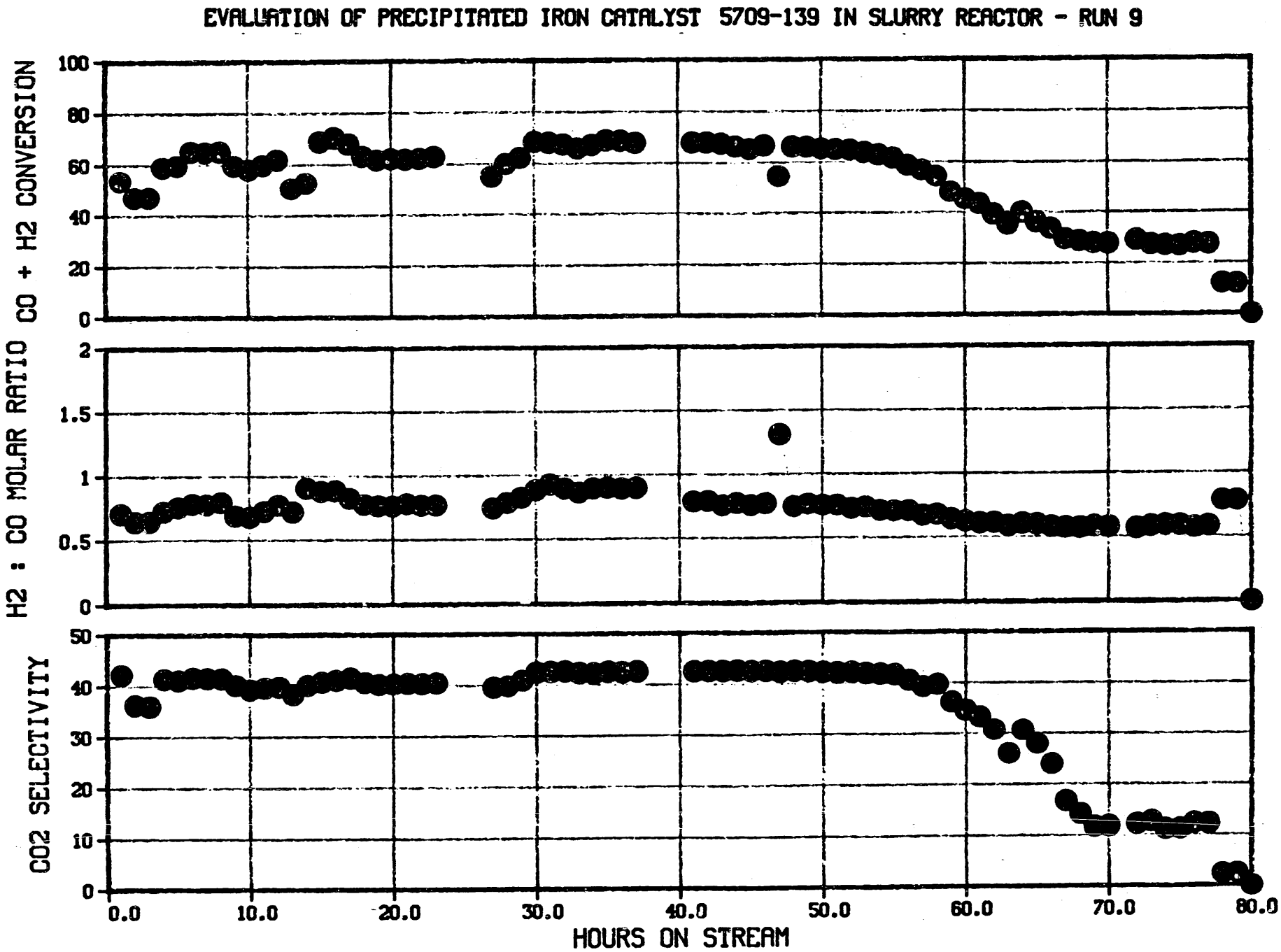

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 9
CO + H2 CONVERSION
H2 : CO MOLAR RATIO
CO2 SELECTIVITY
HOURS ON STREAM
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0

FIGURE 18

EVALUATION OF PRECIPITATED IRON CATALYST 5709-139 IN SLURRY REACTOR - RUN 9

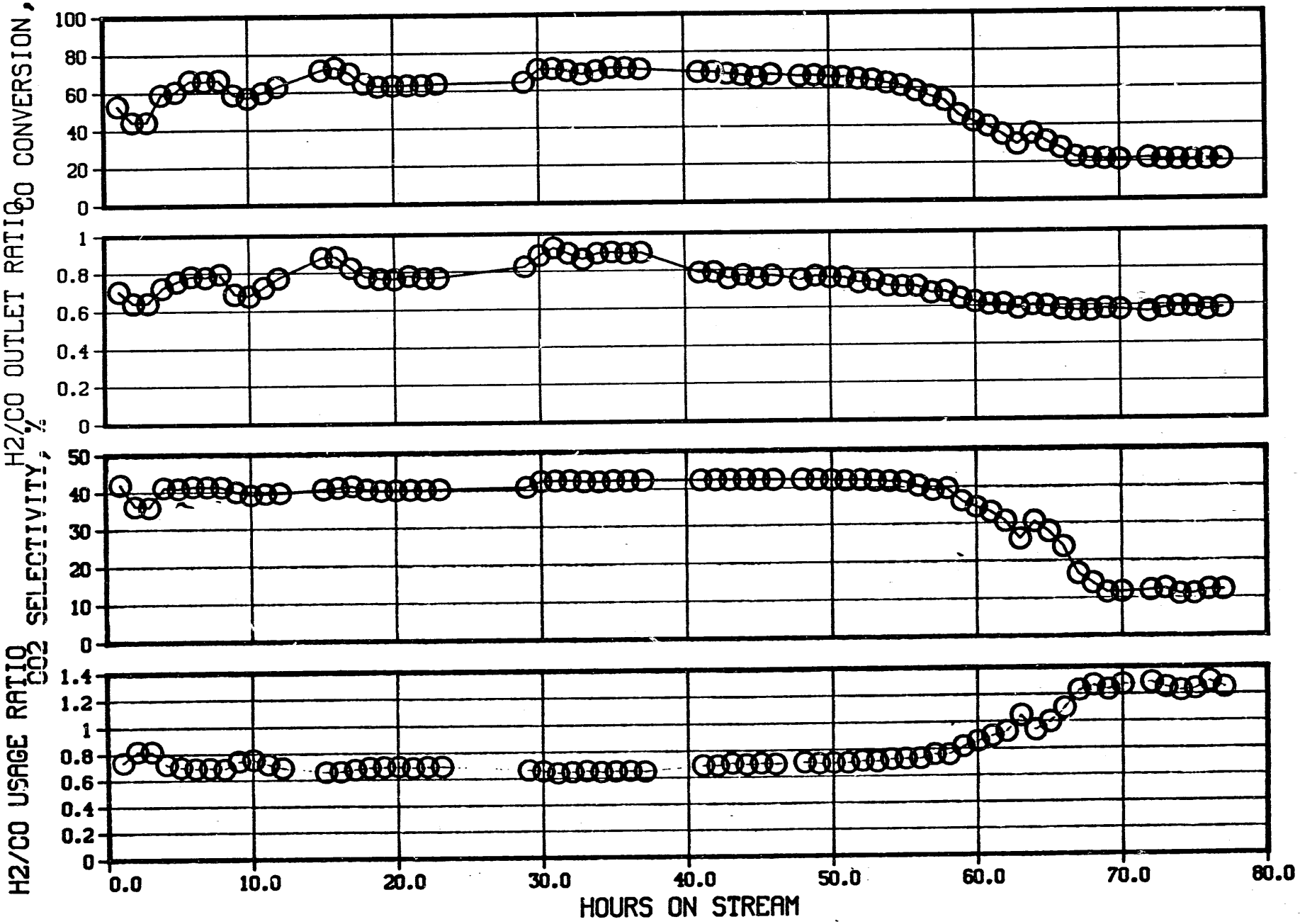
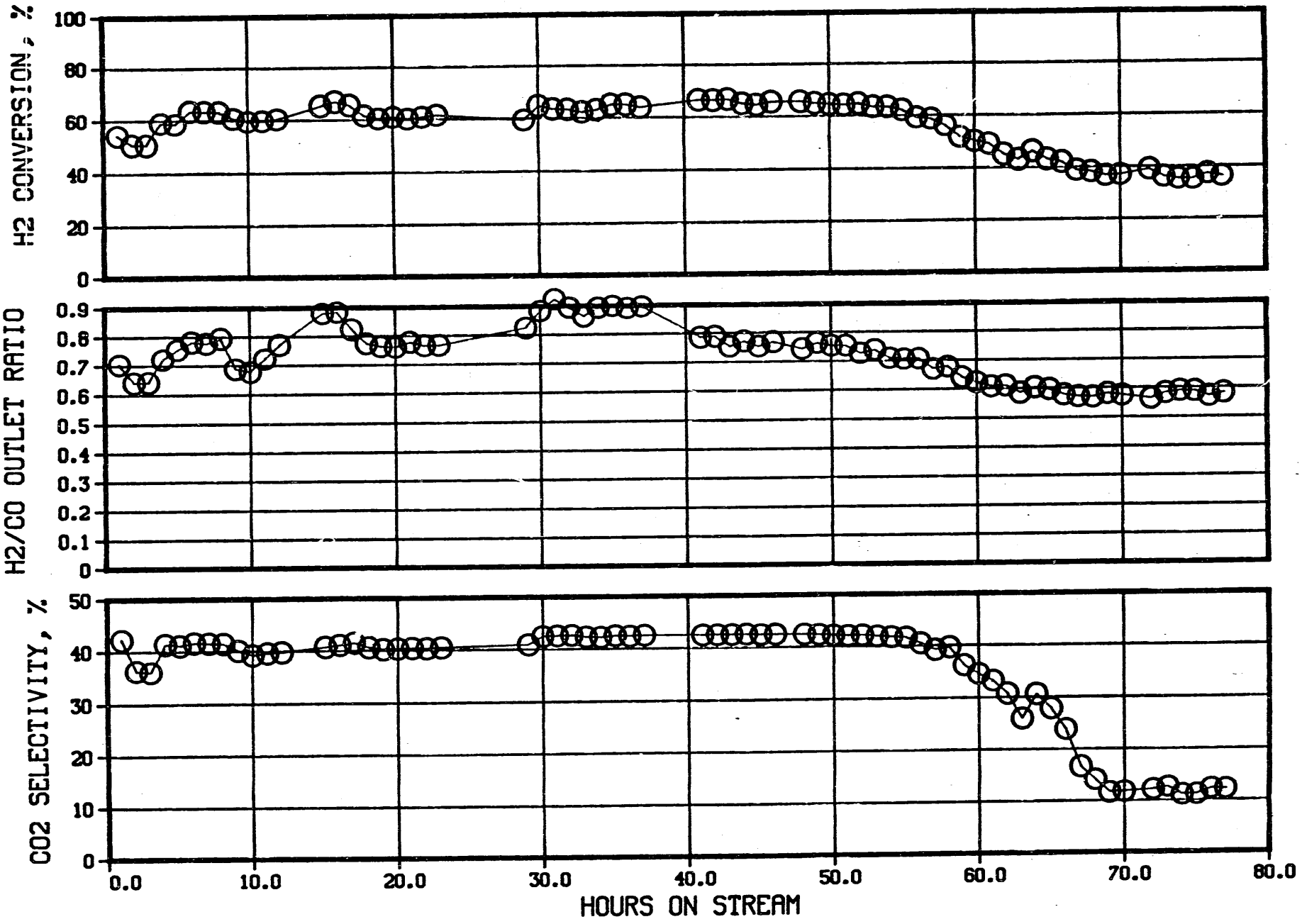


FIGURE 19

EVALUATION OF PRECIPITATED IRON CATALYST 5709 139 IN SLURRY REACTOR - RUN 9



DATE
FILMED
7/27/92