LIQUEFACTION CONTRACTORS' REVIEW MEETING
September 3-5, 1991

ABSTRACT

TITLE: Technology Development for Iron Fischer-Tropsch Catalysts

AUTHORS: Hayim Abrevaya (Principal Investigator), Robert R. Frame, William M. Targos

INSTITUTION: UOP
25 E. Algonquin Road
Des Plaines, Illinois 60017

CONTRACT NO: DE-AC22-90PC90055

PERIOD OF PERFORMANCE: 09/28/1990 to 09/28/1993

OBJECTIVES:

- To develop a technology for the production of active and stable iron Fischer-Tropsch catalysts for use in slurry-phase synthesis reactors.

- To develop a scale-up procedure for large-scale synthesis of such catalysts.

ACCOMPLISHMENTS AND CONCLUSIONS:

- A catalyst test method was developed in the slurry autoclave reactor. The test conditions were set at 265 C, 21 atm, 0.7 H_2: 1 CO ratio, 2.4 NL/hr/g Fe space velocity, and 20% catalyst loading in the slurry. A baseline precipitated iron catalyst was tested four times under these operating conditions to verify reproducibility of performance. During these four tests, at 100 hr on-stream, the $CO+H_2$ conversion was 78 +/- 3%, and the methane and ethane (C_1+C_2) selectivity was 5.4 +/- 0.4%. These results show satisfactory reproducibility of catalytic performance. The $CO+H_2$ conversion and C_1+C_2 selectivity lined out at 70% and 6%, respectively, after 300 hr on-stream for the baseline catalyst.

- A new series of iron catalysts has recently been prepared and is being tested in an attempt to improve C_1+C_2 selectivity. One of these catalysts showed about 69% $CO+H_2$ conversion and 5% C_1+C_2 selectivity after line-out. Although these results are in the proper direction, in order to meet the minimal performance targets, the C_1+C_2 selectivity needs to be further reduced to 4%, and the activity needs to be increased by 23%.

PLANS:

- Complete the evaluation of the new series of iron catalysts aimed at improving the C_1+C_2 selectivity.
- Assess the reproducibility of catalyst preparation by preparing an iron catalyst three times, and then testing these catalysts.
- Clarify the effect of various activation treatments on the performance of iron catalysts.
- Evaluate new precipitated iron catalyst formulations.
- Synthesize various iron phases and test.
- Scale up the currently used precipitation procedure for large -scale synthesis of iron catalysts.

INTRODUCTION

Experimental work conducted under a four-year contract (DE-AC22-87PC-79812) on iron Fischer-Tropsch catalysts was summarized during the 1990 Indirect Liquefaction Contractors' Review Meeting. (1) First, a catalyst preparation procedure was established and a baseline catalyst was developed. This baseline catalyst (752R-16B5A) was used for identifying a viable testing procedure in the slurry autoclave reactor. The baseline catalyst was evaluated in the autoclave reactor and was found to be short of activity and selectivity targets. This year, under a new contract, work on developing iron catalysts for Fischer-Tropsch synthesis continued. This report summarizes the development of a catalyst test method, the evaluation of a new iron catalyst, and discussion of various techniques for characterization of iron catalysts.

EXPERIMENTAL

Catalyst preparation and testing procedures and conversion and selectivity calculations have been described previously. [1]

RESULTS AND DISCUSSION

Catalyst Test Method Development with Baseline Iron Catalyst

To develop a catalyst test method, the baseline iron catalyst was evaluated under different process parameters. These parameters included temperature, pressure, and the nature of the slurry medium.

In a slurry autoclave reactor, the Fischer-Tropsch reaction rate is adversely affected by an increase in the conversion level. Figure 1 shows the product of space velocity and $CO+H_2$ conversion plotted as a function of conversion for the baseline iron catalyst, as discussed during the 1990 Contractors' Review Meeting. This relation may be explained by low partial pressures for reactants and high partial pressures for products at high conversion. Therefore, compared to slurry bubble column work conducted in other laboratories, relatively higher pressures and higher temperatures are required to increase the reaction rate and to achieve high conversion in a slurry autoclave reactor. For this stage of the program, a catalyst testing temperature of 265 C and a pressure of 21 atm were chosen. The slurry medium was changed from C_{32} paraffin wax (Humphrey Chemical) to C_{30} oil (Ethyl Corporation) because of the presence of bromine impurity in the C_{32} wax. Other conditions were 0.7 H_2: 1 CO feed, 2.4 NL/hr/g Fe (normal liter per hour per gram iron) space velocity, and 20 weight % catalyst in slurry. During the first 12 hr, the catalyst was activated at 280 C, 11 atm, and 2.0 NL/hr/g Fe.

The baseline iron catalyst (752R17B7A) was tested four times under the conditions described above (Figures 2-5). The initial $CO+H_2$ conversion ranged between 81 and 83% for all tests. At 100 hr on-stream, the average $CO+H_2$ conversion was 78%. A statistical analysis of the data indicates that the reproducibility of the conversion data with 90% confidence was within +/- 3%. At 100 hr on-stream the average methane and ethane selectivity was 5.4%. The reproducibility of selectivity data with 90% confidence was +/- 0.4%. The H_2:CO usage ratios in these tests ranged between 0.55 and 0.57. These results show satisfactory reproducibility for the current stage of the work.

Lined-out Performance of Baseline Catalyst

The $CO+H_2$ conversion lined-out at 70% after 200 hr on-stream for the baseline catalyst (Figure 6). The C_1+C_2 selectivity seems to have lined-out at 6% after 300 hr (Figures 8-10). While this selectivity is similar, this catalytic activity is two times higher relative to the performance of the baseline iron catalyst reported last year. Under Contract DE-AC22-87PC-79812, 70% conversion was obtained with the baseline catalyst at 1.2 NL/hr/g Fe, 265 C and 21 atm (Figure 1). The activity difference may be explained by the elimination of bromine impurity from the new slurry medium. However, the catalyst histories prior to the establishment of specific test conditions were different, and this difference may also have influenced the results.

New Iron Catalyst

A new series of iron catalysts have been recently prepared. In this series, the amount of one of the catalytic components was progressively varied relative to its value in the baseline catalyst. One of these catalysts, 752R19B9C, was compared with the baseline iron catalyst. The test lengths were kept relatively long to compare the lined-out performances: 282 and 380 hr, respectively, for the new and baseline iron catalysts (Figures 6-10). The $CO+H_2$ conversion for the baseline iron catalyst gradually decreased from 81% to 70% during the first 200 hr, after which there was no further decline; the lined-out methane and ethane selectivity was 6%. The conversion for the new iron catalyst increased during the initial part of the test and lined-out at about 69% $CO+H_2$ conversion after 10 hr on-stream; the methane and ethane selectivity was 5%. The H_2:CO usage ratios were similar for both catalysts. These results show that the new iron catalyst may have superior selectivity and similar activity relative to the baseline catalyst tested under this new contract. However, other experimental catalysts in the same series need to be evaluated to assess these results.

Sequential CSTR Model

In an attempt to extrapolate the slurry autoclave results with the new iron catalyst to a slurry bubble column reactor, a sequential CSTR (continous stirred tank reactor) model was developed. According to this model, the slurry bubble column reactor was treated as several sequential CSTRs with equal volume (Figure 11).

The mass balance equations for the case with 3 CSTRs are shown here as an example.

1. $F*X_1=R(X_1)*W$
2. $F*\ X_2-X_1\ =R(X_2)*W$
3. $F*\ X_3-X_2\ =R(X_3)*W$

In these equations, F is the feed flow rate to the first reactor in NL/hr, X is the cumulative $CO+H_2$ conversion in each reactor, R(X) is the reaction rate in NL/hr/g Fe as a function of conversion and W is the weight of iron in each reactor. The subscripts refer to the reactor number.

The cumulative conversion in the final reactor, X_3, was 0.88. The feed rate, F, to the first reactor was 141 Nl/hr. The relation between reaction rate and conversion, R(X), was not available for the new iron catalyst. However, since the activity of the new iron catalyst was similar to the baseline catalyst under these new test conditions, twice the R(X) measured under the old test conditions for the baseline catalyst (see Figure 1) was used as an approximation to the reaction rate under the new test conditions. The remaining three unknowns, X_1, X_2 and W, were solved by using the three mass balance equations and a trial-and-error procedure. The feed rate to the first reactor was then divided by the total weight of iron in the three reactors to calculate the overall space velocity. The results for 1, 2, 3 and 4 sequential CSTRs are summarized in Table 1.

Table 1
Space Velocities for 88% $CO+H_2$ Conversion
Feed=141 NL/hr

Number of CSTR's	Total Weight of Iron, gram	Overall Space Velocity, NL/hr/g Fe
1	157	0.90
2	89.2	1.59
3	76.5	1.85
4	73.3	1.93

According to this model, the space velocity required for 88% conversion with the new iron catalyst does not show very significant variations beyond 3 CSTRs. Assuming the slurry bubble column reactor can be modelled by 3 sequential CSTRs, then the ratio of predicted space velocity to target space velocity is 0.77, which makes the new iron catalyst 23% short of the minimal activity target for the program. During the 1990 Contractors' Review Meeting, methane and ethane selectivity was also reported to vary with the conversion level. [1] For 3 sequential CSTRs, calculations show that the new iron catalyst will result in approximately 5%

methane and ethane selectivity at 88% conversion. The minimal target selectivity for methane and ethane is 4%, which indicates that further selectivity improvements are necessary.

Catalyst Characterization

The iron in fresh catalysts is predominantly in the form of Fe_2O_3. During Fischer-Tropsch synthesis, iron transforms into Fe_3O_4 (magnetite) and into iron carbide(s). In this program, the plan is to use Mossbauer spectroscopy, x-ray diffraction (XRD), and magnetic susceptibility measurements to characterize the bulk phases that are present. However, the surface phases may be different than the bulk, and therefore, alternate characterization techniques that are surface sensitive, like x-ray photoelectron spectroscopy, need to be used as well. Finally, the catalyst surface can be characterized by examining some of the key elementary steps such as CO dissociation and carbon hydrogenation.

Recently, the baseline iron catalyst was examined by magnetic susceptibility after exposure to synthesis gas for various periods of time. Several iron oxide and iron carbide reference compounds are currently being examined in an attempt to interpret the measurements with the iron catalyst. Mossbauer spectroscopy and XRD work have also been initiated on these iron catalyst samples. Future work on these samples will also include surface characterization.

REFERENCES

1. H. Abrevaya, W.M.Targos and M.J.Cohn, "The development of a Stable Iron Catalyst", Indirect Liquefaction Contractors Review Meeting, Pittsburgh, 1990.

FIGURE 1

Effect of Conversion on Reaction Rate

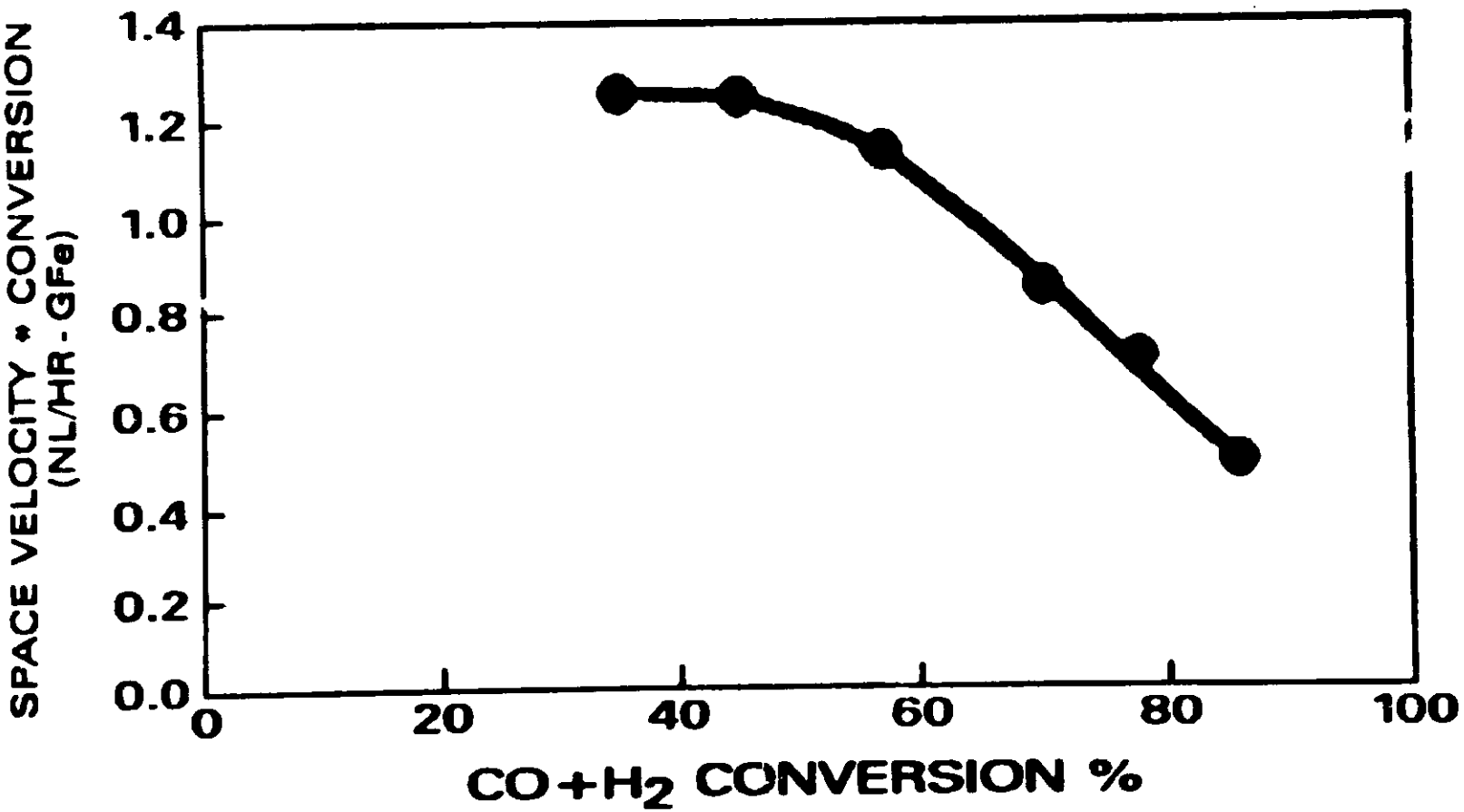


Figure 2

REPRODUCIBILITY OF CATALYTIC PERFORMANCE

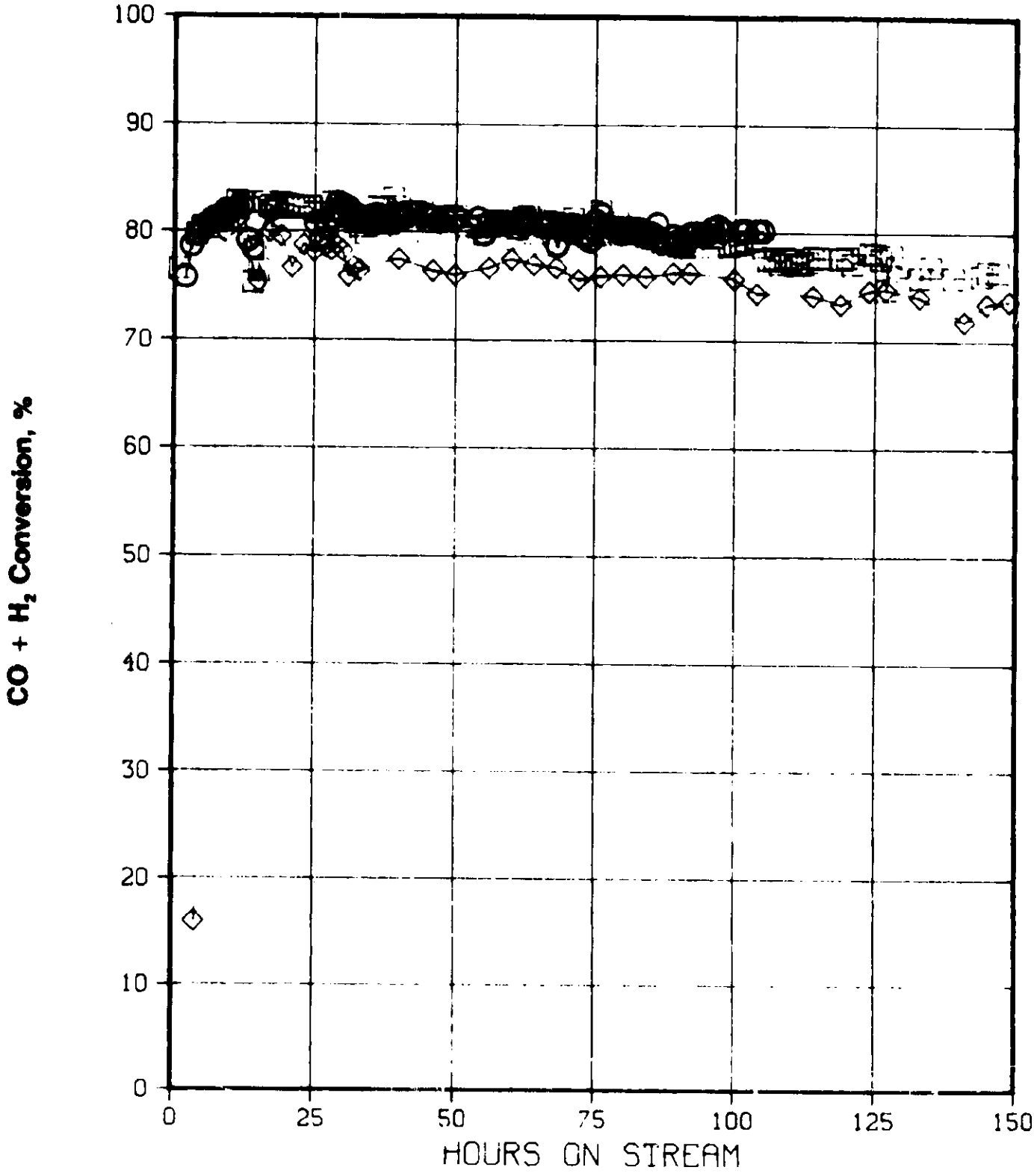


Figure 3

REPRUDUCIBILITY OF CATALYTIC PERFORMANCE

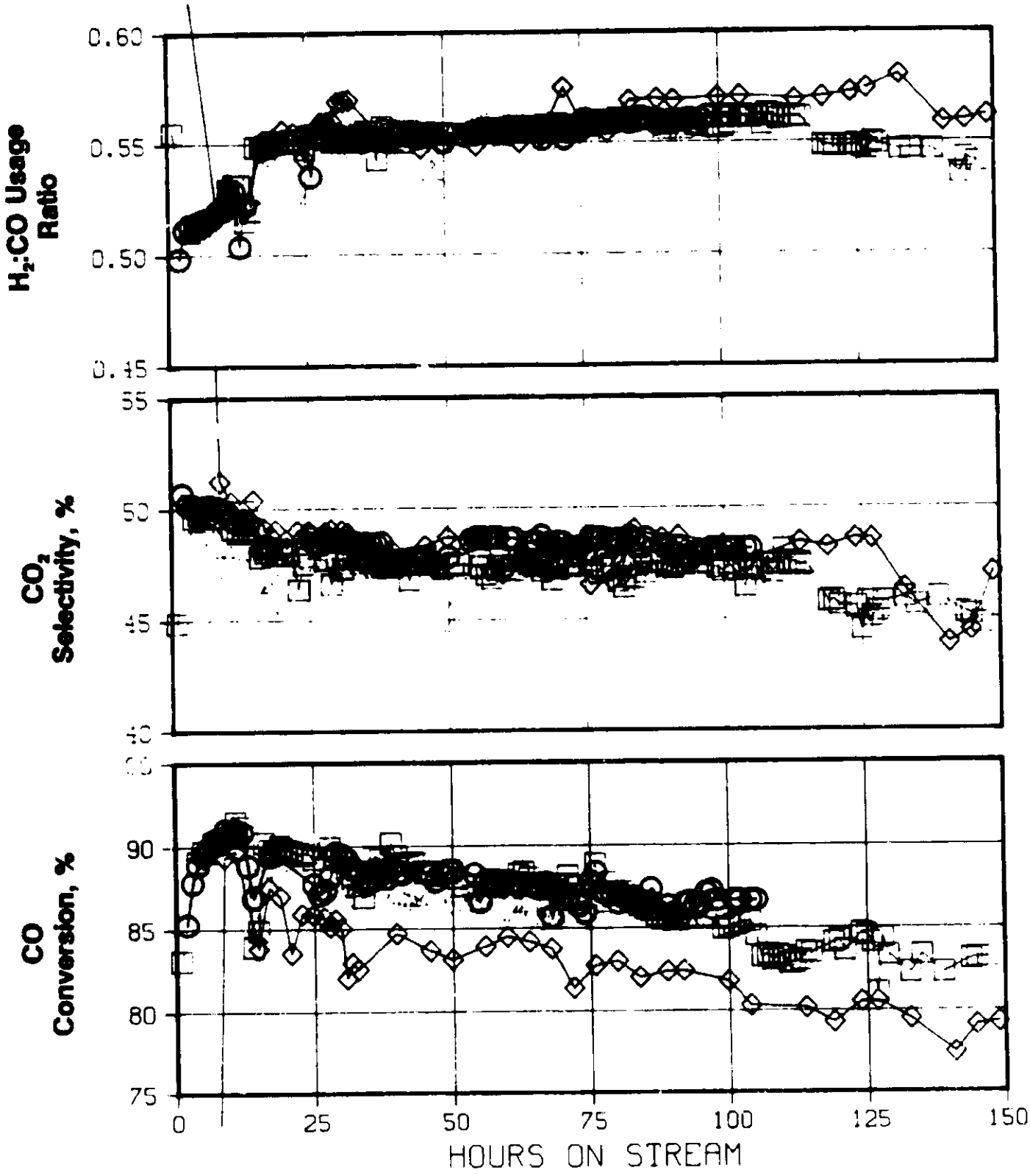


Figure 4

REPRUDUCIBILITY OF CATALYTIC PERFORMANCE

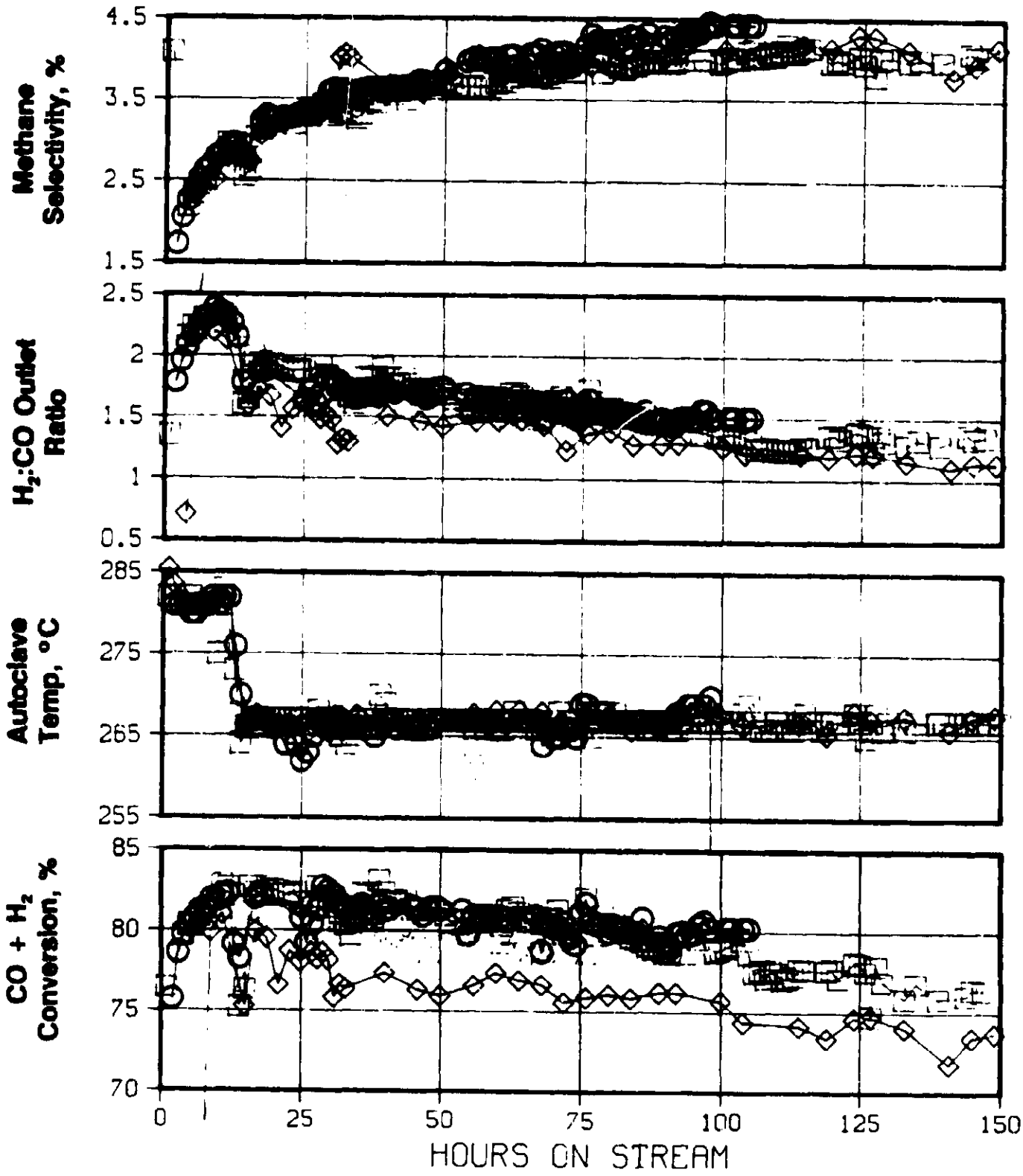


Figure 5

REPRUDUCIBILITY OF CATALYTIC PERFORMANCE

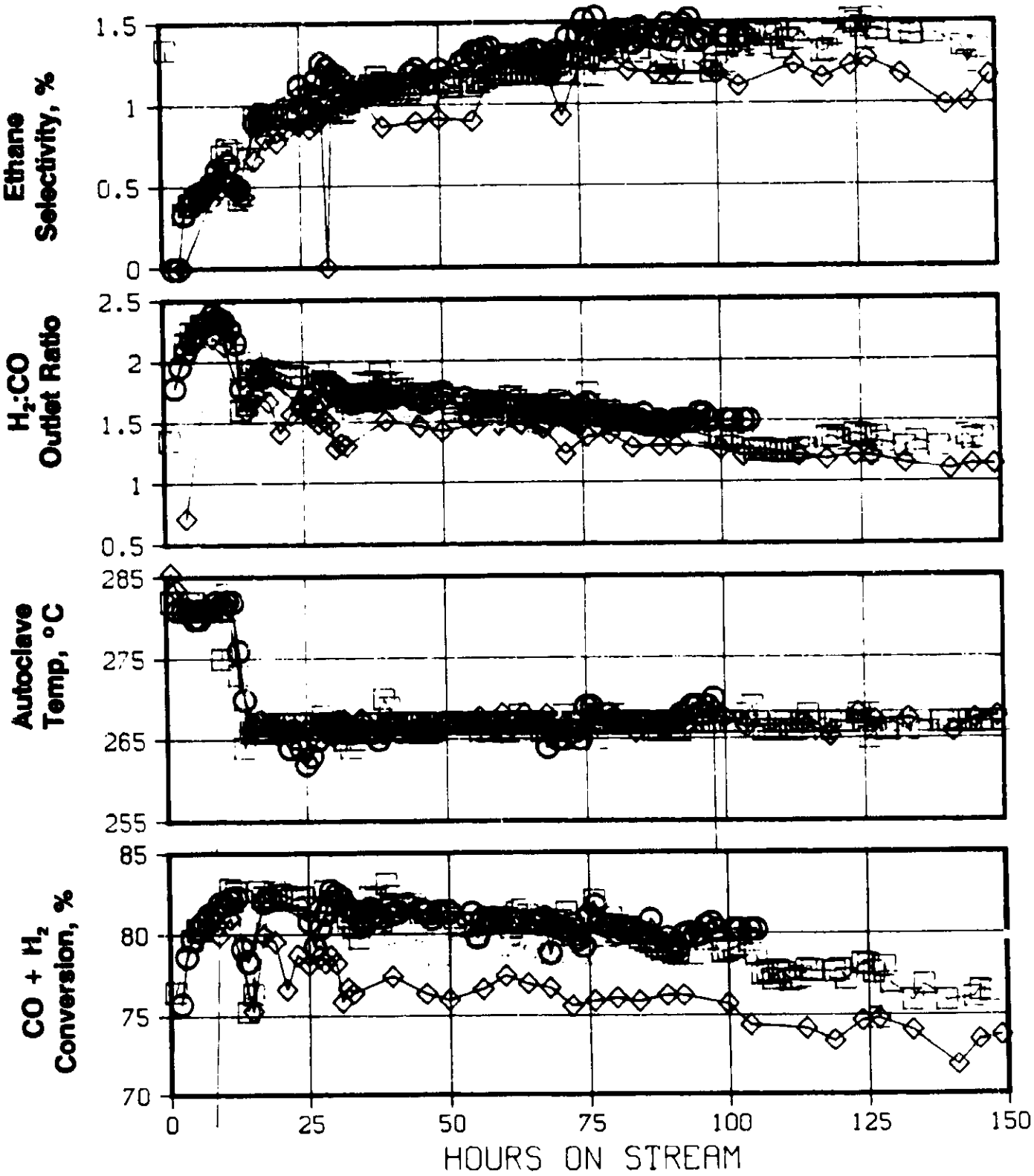


Figure 6

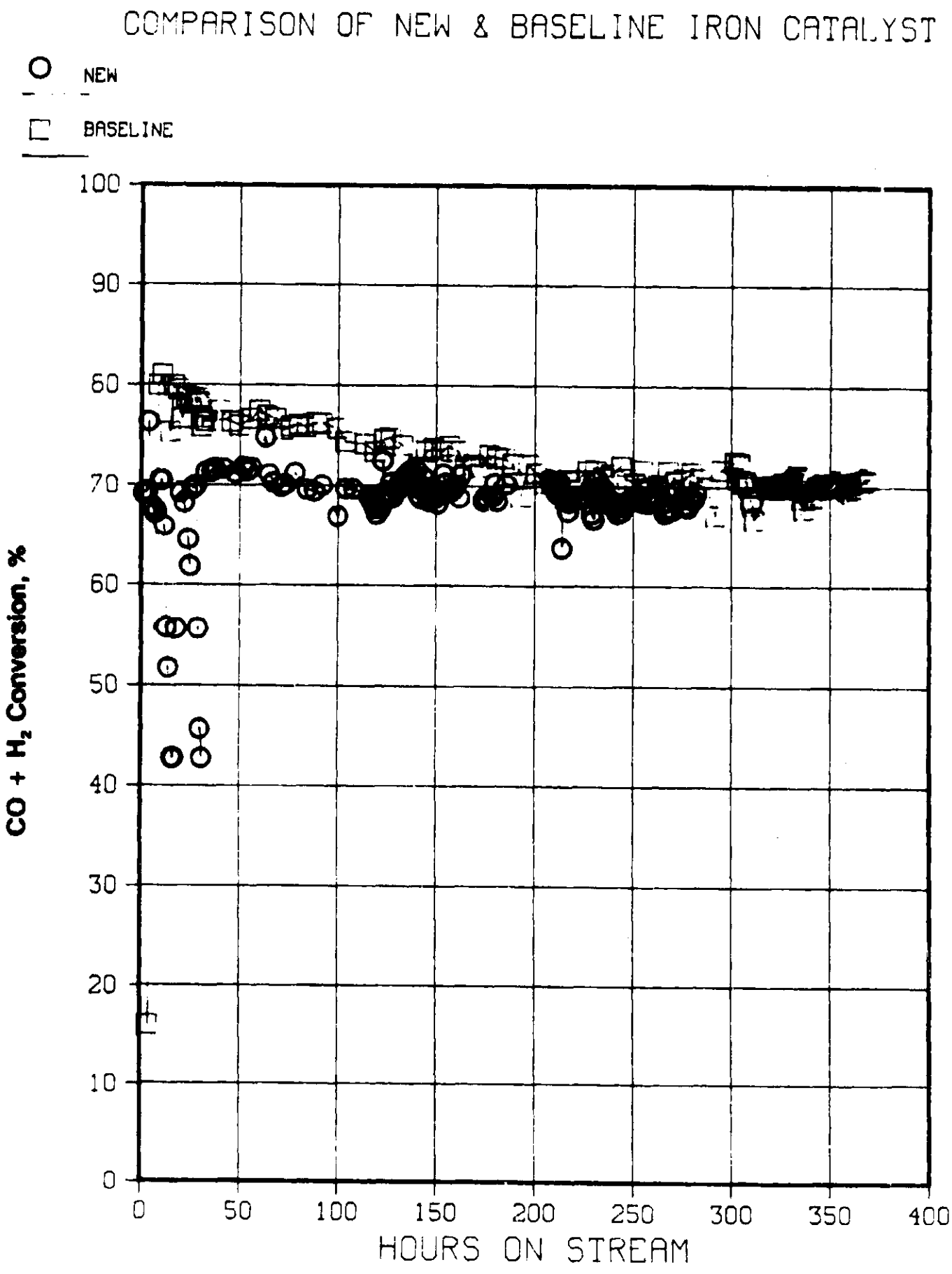

COMPARISON OF NEW & BASELINE IRON CATALYST
NEW
BASELINE
CO + H2 Conversion, %
HOURS ON STREAM
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400

Figure 7

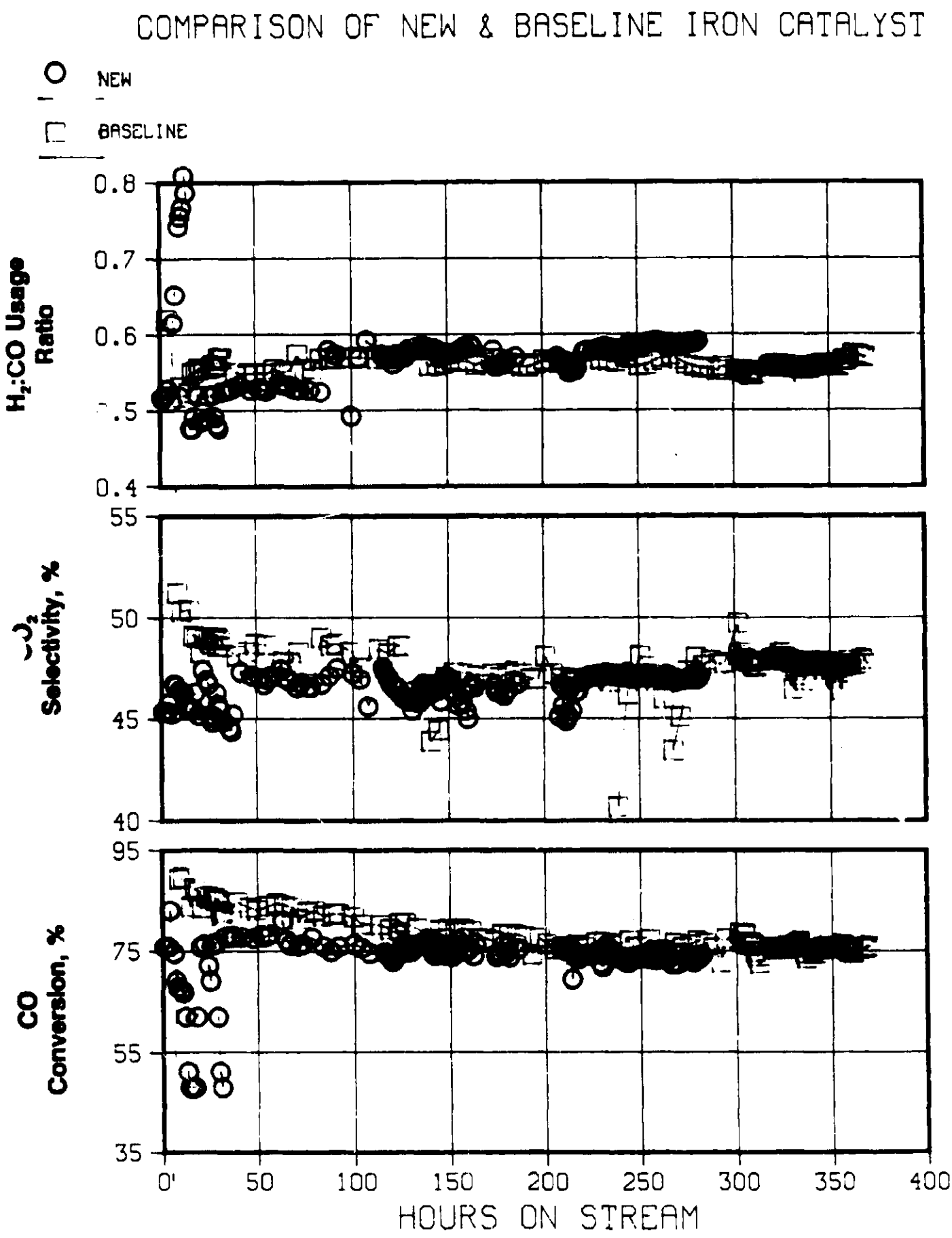

COMPARISON OF NEW & BASELINE IRON CATALYST
NEW
BASELINE
H2:CO Usage Ratio
0.8
0.7
0.6
0.5
0.4
CO2 Selectivity, %
55
50
45
40
CO Conversion, %
95
75
55
35
0
50
100
150
200
250
300
350
400
HOURS ON STREAM

Figure 8

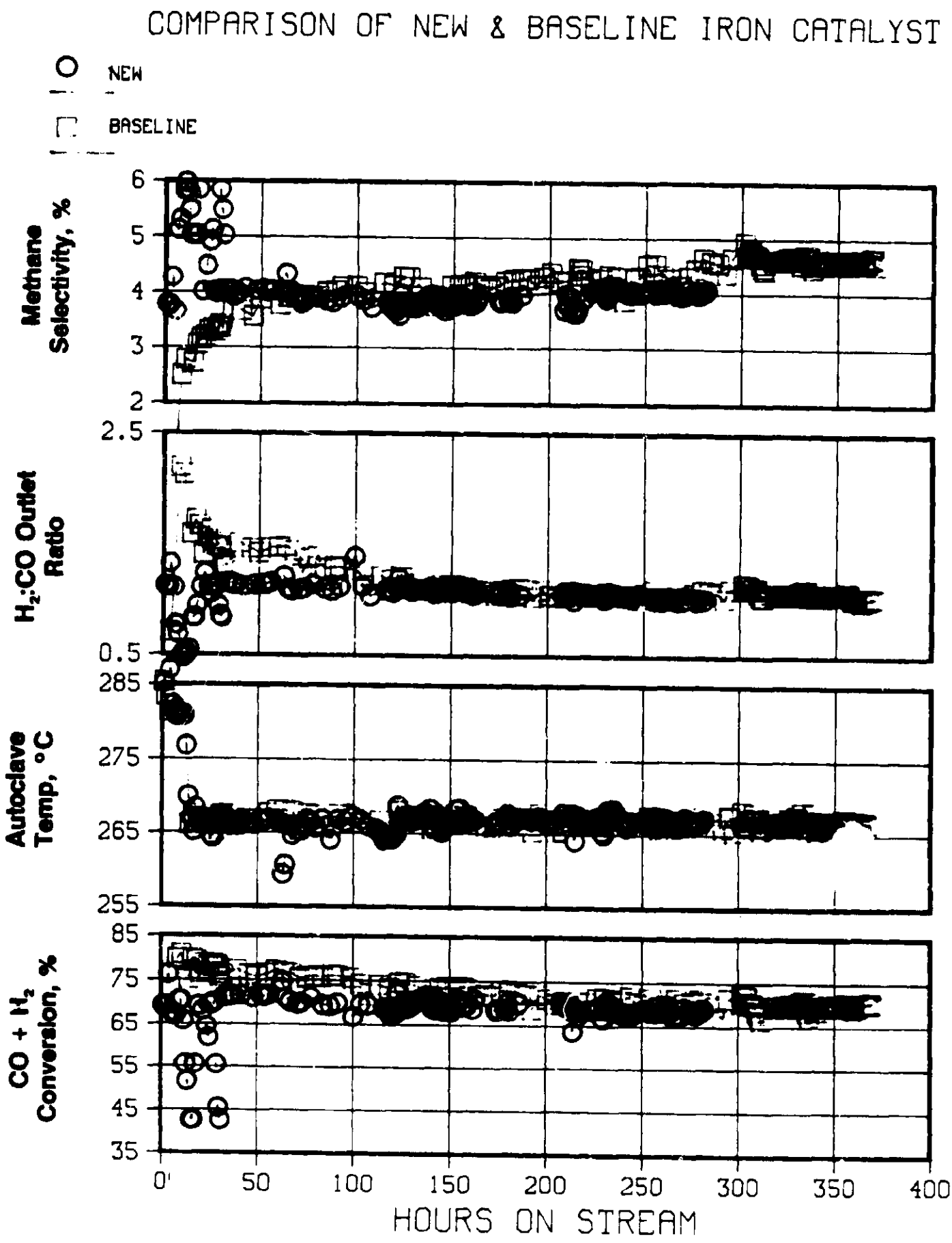

COMPARISON OF NEW & BASELINE IRON CATALYST
NEW
BASELINE
Methane Selectivity, %
6
5
4
3
2
H2:CO Outlet Ratio
2.5
0.5
Autoclave Temp, °C
285
275
265
255
CO + H2 Conversion, %
85
75
65
55
45
35
0
50
100
150
200
250
300
350
400
HOURS ON STREAM

Figure 9

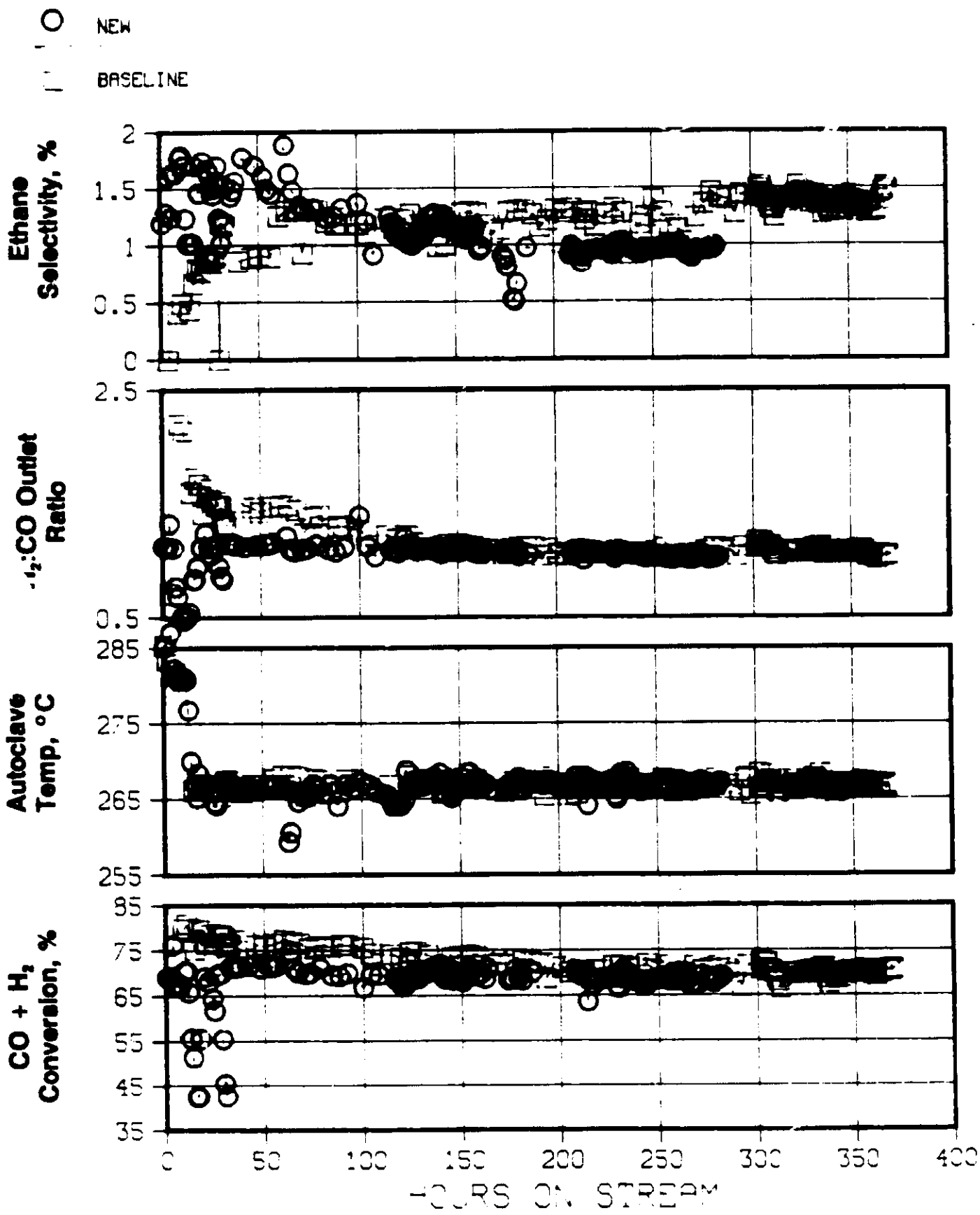

COMPARISON OF NEW & BASELINE IRON CATALYST
NEW
BASELINE
Ethane Selectivity, %
2
1.5
1
0.5
0
H_2:CO Outlet Ratio
2.5
0.5
Autoclave Temp, °C
285
275
265
255
CO + H_2 Conversion, %
85
75
65
55
45
35
0
50
100
150
200
250
300
350
400
HOURS ON STREAM

Figure 10

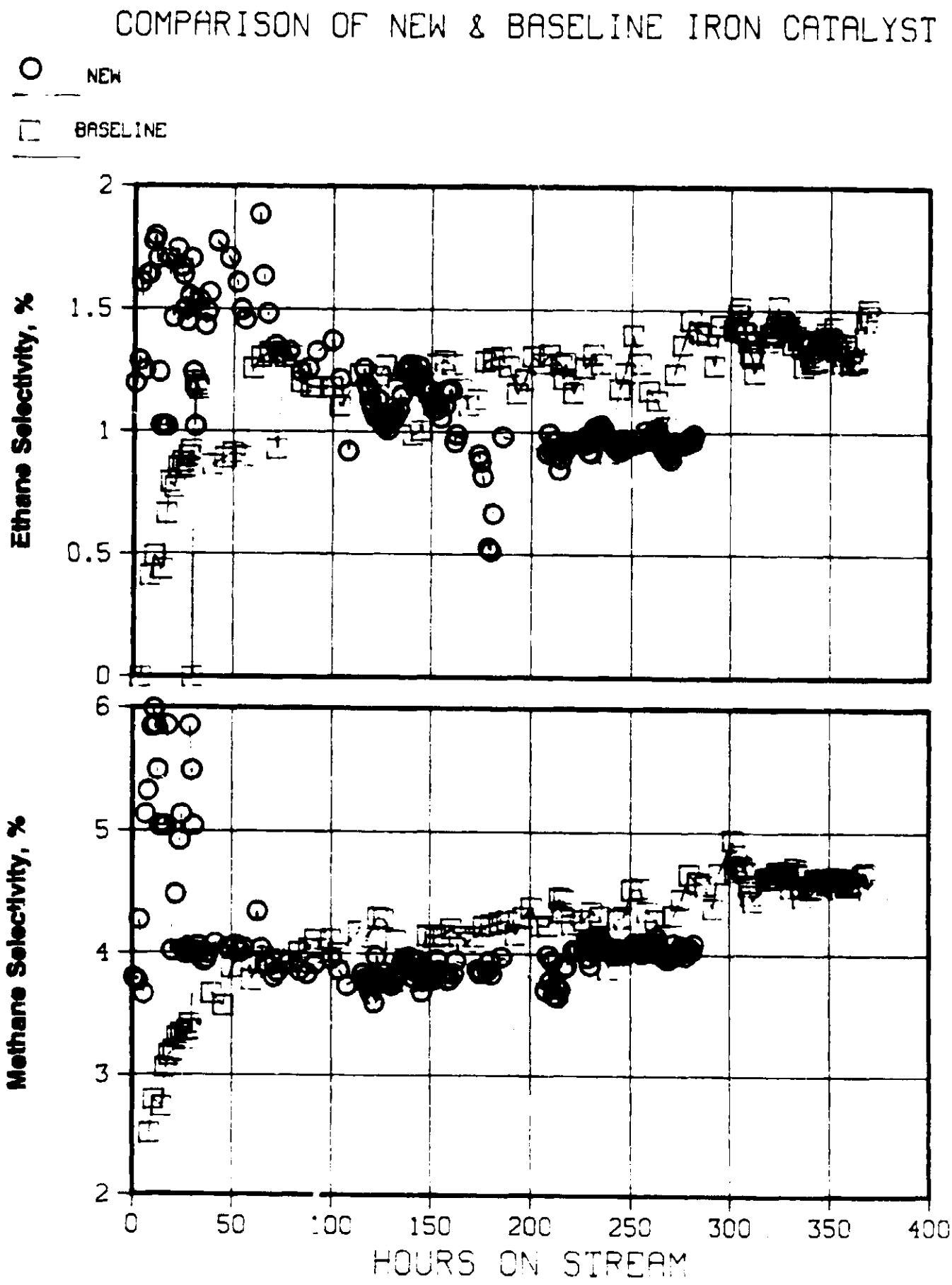
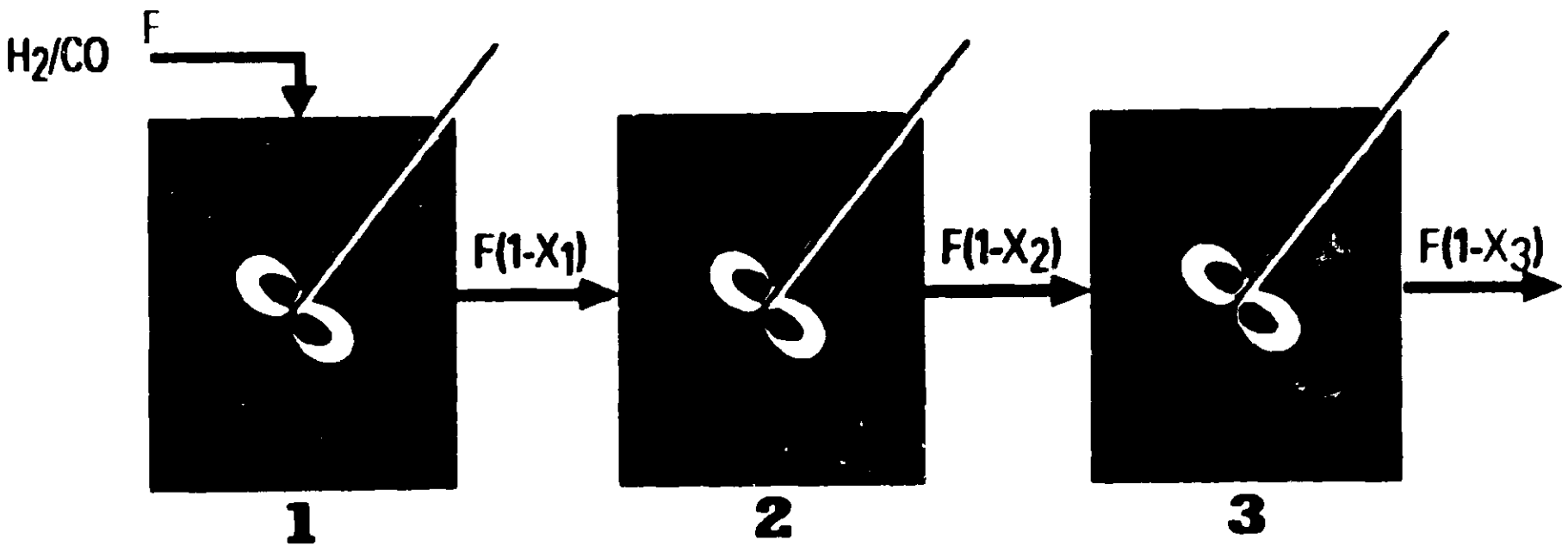

COMPARISON OF NEW & BASELINE IRON CATALYST
NEW
BASELINE
Ethane Selectivity, %
2
1.5
1
0.5
0
Methane Selectivity, %
6
5
4
3
2
0
50
100
150
200
250
300
350
400
HOURS ON STREAM

FIGURE 11

CSTR-in-Series Model



F: NL/HR X: CONVERSION W: G Fe R: REACTION RATE (NL/HR-G Fe)

1. $F*X_1=R(X_1)*W$ 2. $F*[X_2-X_1]=R(X_2)*W$

3. $F*[X_3-X_2]=R(X_3)*W$