Space Velocity:

The design space velocity calculated from the data submitted in the Case 6 design specifications is 2520 V/HR/V. These specs. show a horizontal reactor however and later, if my memory is correct, as changes were made in the design 2200 was consistently referred to as the design space velocity.

In actual practice the bed density has been found to run much higher than the 100#/c.f. predicted in design. It actually is nearer 150 at Brownsville and about 140 at Montebello.

The present reactors can probably accomodate a bed beight of about 17 ft. which, with an average free area between the tubes of 187 sq. ft. amounts to a total catalyst volume of 3180 C.F. or a space velocity with the design rate of 5,000,000 SCFH of Syn. gas of 1570 V/HR/V. At 150#/c.f. catalyst density, this bed height requires about 240 tons of catalyst which is the amount now normally used for a full load.

Although the ultimate goal is to operate at 1600 space velocity the present synthesis gas output with one oxygen plant in service is only 3 million SCF of syn. gas instead of the design value of 5 million. At this actual rate therefore the space velocity required per reactor is about 960 SCF of Gas/Hr/CF of catalyst bed.

Discussion of Fig.C.

It will be noted from Fig. C that there is a long way to go before Brownsville results will equal those of the pilot units and, what is more important, the pilot units have almost as far again to go to reach the desired goal at the ultimately desired space velocity of 1600.

It will be noted also from Fig. C that if a line is drawn thru the best of the Brownsville high space velocity data and extended to zero space velocity the yields would still not be as good as those obtained on the pilot units at 960 space velocity.

Fig. D Space Velocity vs C_3 + Yield for Averaged Data

In plotting the points on Fig. C it was observed that in many runs the yields in the first day's operation were substantially higher than those for succeeding days at the same operating conditions. This effect was obscured in Fig. C because of the random distribution of the points representing succeeding days. Furthermore in nearly all runs the space velocity was increased only after several day's operation (time required to get the second oxygen plant in service). We therefore averaged the data for periods where operating conditions were kept constant leaving the first day's operation separate and obtained the following plot Fig. D. On this plot we have shown besides each point the number of days represented by the point and we have put a ring around each pt. representing the first day.

On this graph the abscissa should have been made longer to permit showing all the points at very high space velocities in Run 17. These however are simply an extension of the graph as can be seen thru reference to the individual plot for Run 17.

This is one of the most important graphs in this report. It correlates well all the recent run data, Runs 11 thru 17, excepting only the first day of Run 16 which covered a 17 1/2 Hr. period but was obviously out of line.

The line thru the Brownsville data shows the combined effect of space velocity and catalyst deactivation. *

*To a certain extent the lower end of the curve, beyond 1000 to 1200 Sp.vel. also may be influenced by total feed inlet temperature but as shown before this temperature actually doesn't change very much (530° F to 415°F) and therefore its effect on this graph should not be pronounced.

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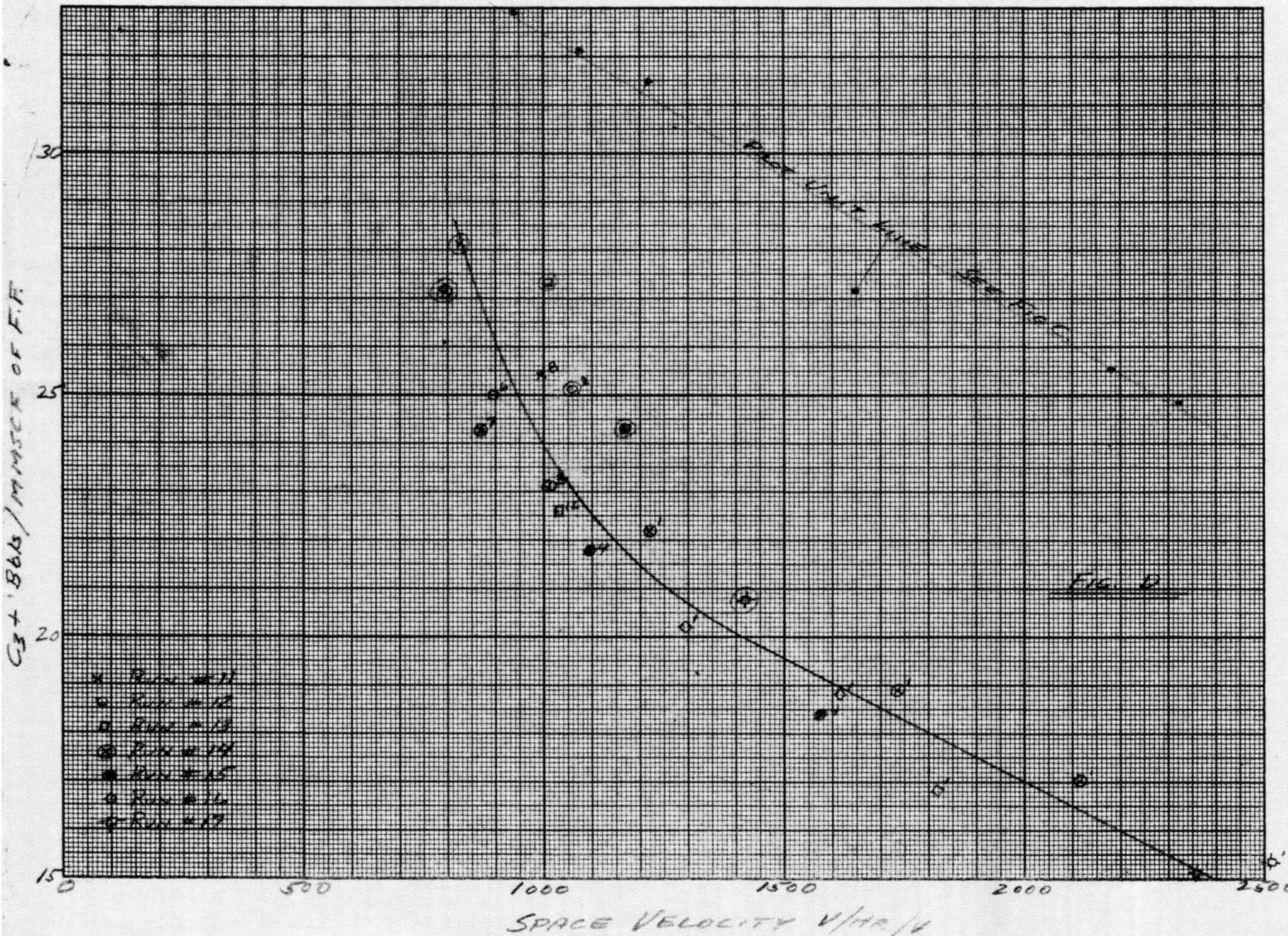


The pilot unit line on the other hand since it was based on the first few days operation of several different runs (see Table V p. 21 PR 37P) shows the effect predominantly of space velocity alone.

From the relative position of the first day points the Brownsville catalyst deactivates very rapidly at the very beginning of each run. It will be noted also that if the steep portion of the curve were to be extrapolated to, say, the first hour's operation, the yields would very likely be right up there with those obtained at the same space velocity on the pilot units.

Moving down The Brownsville line to the points representing the largest number of days (at about 1000 space velocity) it will be noted that the slope is still very steep until we get to space velocity of about 1200 beyond which the line parallels the true effect of space velocity on the pilot units. This steep intermediate portion of the curve, where most of the data fall, indicates that poisons are entering the system with the gases. A small increase in space velocity increases the rate of poison entering the system so that catalyst activity and yields drop off rapidly. Beyond that, the catalyst is virtually dead anyway and the effect is almost purely one of space velocity alone.

This graph and the previous Fig. C also show that if the initial degree of reduction of the catalyst and catalyst carbiding have any effect at all, the effects are well within the accuracy of the data.

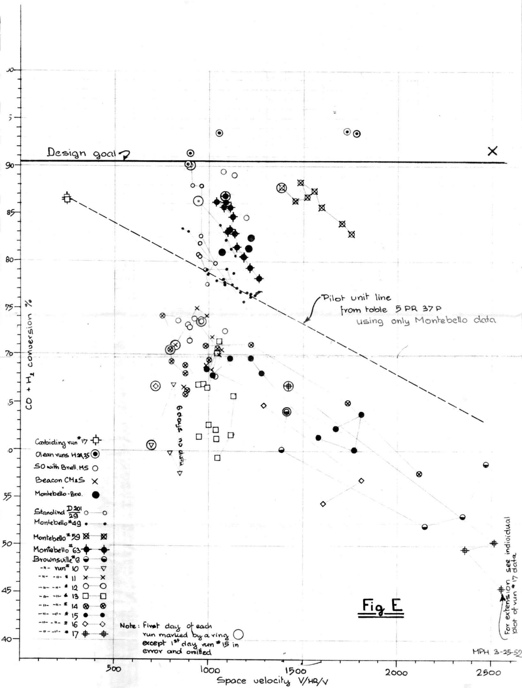
Also since Run 17 made predominantly at very high space velocity because of very low catalyst bed, falls on the curve with other runs of deeper bed where the space velocity was high only because of high thruput instead, Fig. D indicates that at this low level of activity, at least, bed height and therefore probably catalyst contacting efficiency have little to do with the poor conversions, at least not at these low levels of activity.

<u>Fig. E. Space Velocity vs H_2 + CO Conversion:</u>

Fig. E is a plot similar to Fig. C except that H_2+CO conversion is the ordinate instead of the C_3+ yields. This graph like Fig. 1, permits a direct comparison of Brownsville and Pilot Unit data and also shows the H_2+CO conversions obtained at Brownsville at very low space velocity during carbiding operations.

The solid line at 90.4% H_2+CO conversion represents the design goal. It will be noted that the HRI H series runs H-24 & H-25 (⊙) which it will be remembered were made on an 11.5" i.d. reactor with spent CM&S catalyst all fall on or above the goal. The Beacon data (x) with the same catalyst and with Brownsville Mill Scale catalyst also all fall along this line but only one run (7027) was available at low enough space velocity to be shown on this plot. The others were all made at space velocities of 5,000 to 15,000 V/HR/V.

Referring to the Stanolind and Pilot unit data it will be noted that the deactivation with time when using either mill scale or Allan Wood Catalyst at a given space velocity is quite pronounced though much slower than which takes place at Brownsville as shown in Fig. D above. The deactivation in the Stanolind Run #2D with Allan Wood catalyst (O-O) was somewhat more rapid and more consistent than that obtained with the same catalyst at Montebello.



Design goal
Pilot unit line
from table 5 PR 37 P
using only Montebello data
CO + H_2 conversion %
Space velocity V/HR/V
500
1000
1500
2000
2500
90
85
80
75
70
65
60
55
50
45
40
Carbiding run # 17
Olean runs H 24,35
50 with Brall. MS
Beacon CM1S
Montebello-Bro.
Stanolind D201/29
Montebello #49
Montebello #59
Montebello #63
Brownsville #8
-"- run # 10
-"- -"- # 11
-"- -"- # 12
-"- -"- # 13
-"- -"- # 14
-"- -"- # 15
-"- -"- # 16
-"- -"- # 17
6 days no data
Note: First day of each run marked by a ring except 1st day run # 15 in error and omitted
For extension see individual plot of run # 17 data
Fig E
MPH 3-25-52

The Montebello Run #59 (⊠) with spent CM&S catalyst, on the other hand shows a much slower rate of deactivation, if any. A line thru the points for this run is almost parallel to the dotted line showing the effect of space velocity in the Pilot units. This line is the same as that shown on Fig. D above.

It is quite interesting to note that the Brownsville carbiding runs fall exactly on an extrapolation of this space velocity line. This indicates that during carbiding operations when operating with a fresh catalyst and relatively high hydrogen partial pressure The Brownsville Reactor acts just about the same as the Pilot unit reactor. On the other hand it is evident, of course, that this space velocity line does not go thru the best pilot unit results but perhaps represents instead average results with a catalyst that has become somewhat stabilized.

Except for Run #10 and the latter part of Run #13, the plant scale data, at a lower conversion level show about the same effect of space velocity on H_2+CO conversion as does the pilot unit line. As we have seen from Fig. D however this is not the whole story.

Discussion of Figs. 1, 1A & 1B

Figs. 1, 1A & 1B were included at the beginning of the report because they show quite strikingly the differences between Brownsville, pilot unit and laboratory results. They were among the first plots made and all the Brownsville data were included even though we now know that some of these data, notably Runs 5 & 8, are in error. These form the first of a series of graphs where

Brownsville and Pilot unit results are compared with base lines established in the 1947 correlations (EDG Report No.1) from an extremely large number of data obtained at several laboratories.

Since the points are joined in chronological order with rings around the first day of each run, the drift downward to lower H_2 conversion with time is quite evident. It is also clear that the drift on Pilot units is of the same order though slower than that experienced at Brownsville.

With reference to the Pilot unit results it will be noted that the Montebello data fall about where they should with respect to the base lines because the Montebello gas has an H_2/CO ratio of only 1.6 compared to 1.8 for Brownsville and 2.0 for the lab. and the Stanolind Pilot unit runs. This, incidentally, may explain the relatively high selectives for a given H_2+CO conversion consistently reported by Montebello because conversion is always expressed as % of H_2+CO and Montebello has less H_2 to start with.

On the other hand, The Allan Wood catalyst at Montebello apparently results in better selectivity than that obtained with Mill Scale.

It would appear from Figs. 1, 1A & 1B that the problem of raising Brownsville conversions is the same <u>kind</u> of problem as that of raising Pilot unit results to those of the smaller units.

Although a little difficult to see on Fig. 1 & 1A, it will be noted that the drift in activity with time of the spent CM&S catalyst on the Montebello unit was not as great as with Mill Scale.

It was still there however and even with this apparently more stable catalyst periodic reactivations would be required to maintain activity. Such periodic reductions were used on the "1000 Hr. demonstration Run 19-6 with fresh CM&S catalyst at Trenton.

In general it will be observed from Figs. 1, 1A & 1B that all the data, comm'l., pilot unit and lab. fall pretty close to the base lines established in 1947. This is pertinent to succeeding discussions.

H_2 vs CO Conversion - Fig. 2

The following Fig. 2 is a plot of H_2 vs CO Conversion for all the data used in Figs. 1, 1A & 1B except for a few points and Runs 5 & 8 which were discarded above. On this plot the CO Conversions for Run 10 are obviously in error and should be ignored. The nomenclature on this and succeeding plots is the same as in Fig. 1.

The solid lines on this graph are those that were established in the 1947 correlation (EDG Report #1) and the dotted line is an interpolation for Brownsville feed showing where Brownsville data ought to fall.

I strongly believe that this graph is the key to the entire problem. If we can explain why the Brownsville and pilot unit data on Allan Wood and Mill Scale fall below the lines where they should, that is, why the CO disappearance for a given H_2 disappearance is less than it should be, we shall probably have a clear understanding not only of the poor Brownsville yields but also of the reason why the pilot units at Stanolind and Montebello

Do over

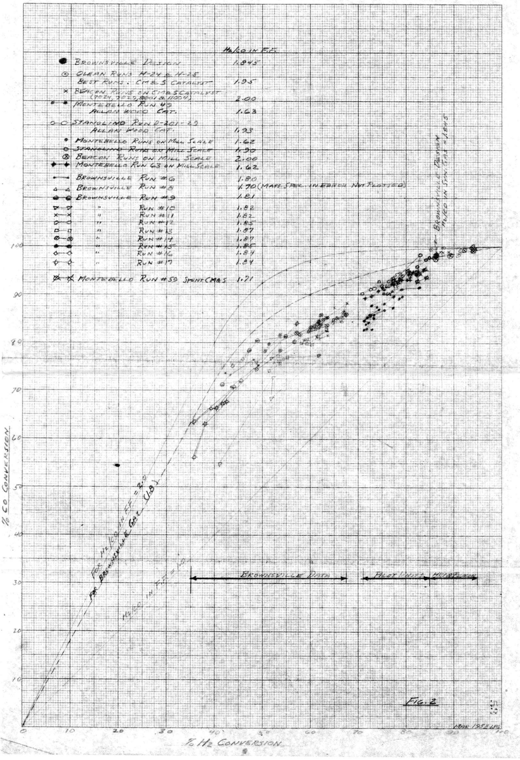


FIG. 2

MAR 1952 LPG

do not check the results obtained on the smaller Beacon units or in the H series runs on CM&S catalyst in the 11 1/2" reactor at Olean. Incidentally, we shall also probably explain the as yet unexplained reason why the HRI 14 and 15 series runs in the 4 1/2" reactor at Olean and the Trenton 19-6 Run also fall below the base lines which were established predominantly by Beacon and HRI H series data in 1947 (see EDG Report #1).

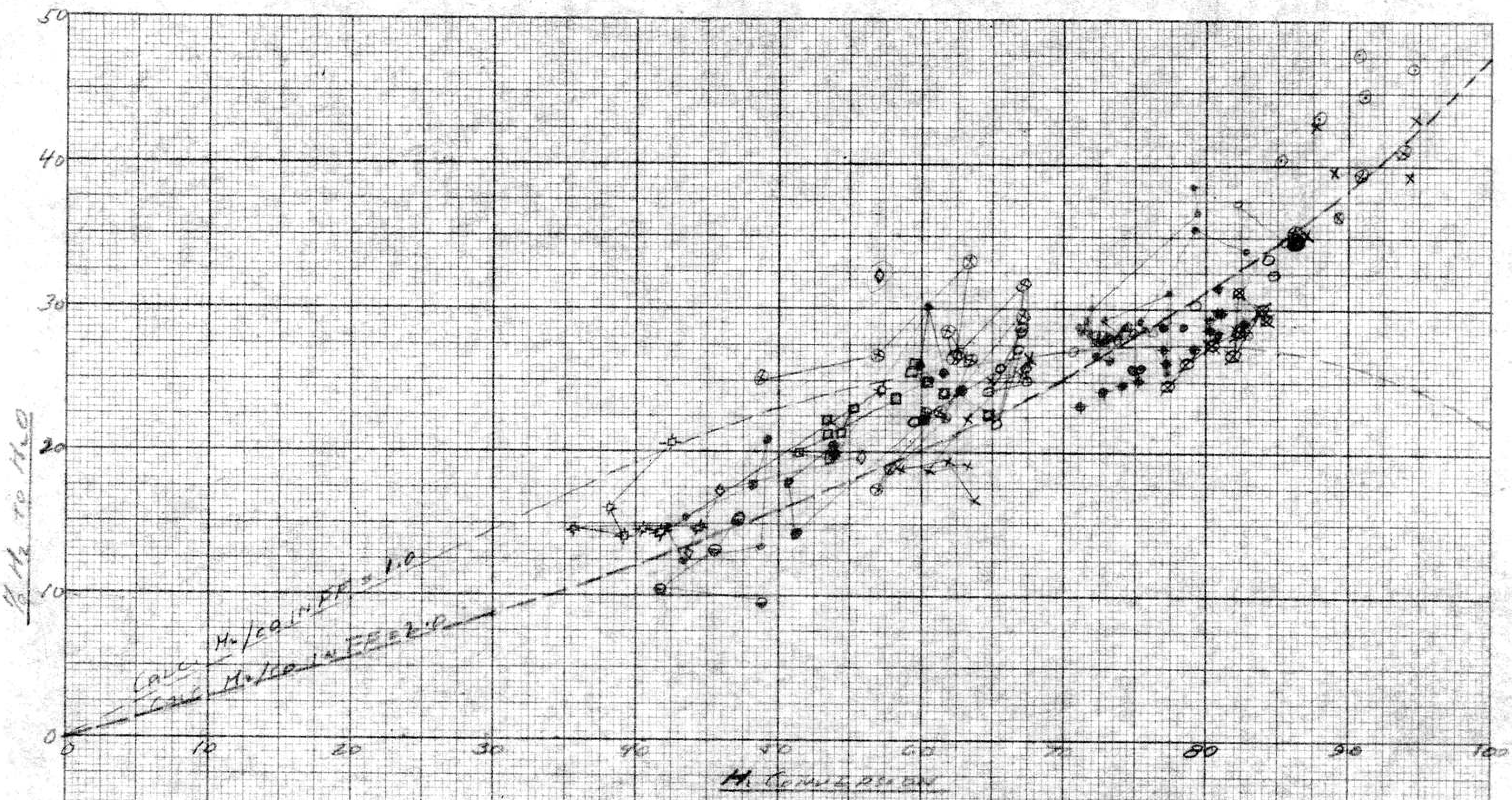
It will be noted that the design point falls on the line. This, plus the fact that Beacon has exceeded the desired H_2 and CO conversions at very high space velocities (up to 15,000) indicates that the goal can be attained.

Before attempting to explain the difficulty, we shall introduce the next plot.

H_2 Conv. vs CO to CO_2 and H_2 to H_2O - Fig. 3

The following Fig. 3 is a plot of all the data, except that previously discarded, showing the relationships between H_2 Conversion and the amount of CO in the fresh feed that went to CO_2 and also the amount of H_2 in the fresh feed that went to H_2O.

The solid lines in the CO_2 plot are, as before, those which were established in our correlation of 1947. The corresponding lines in the H_2O plot are shown dotted because they not only correlated the data well in 1947 but they are actually calculated by oxygen balance assuming that the solid lines in the CO_2 plot on Fig. 3 and the solid lines in H_2 vs CO plot on Fig. 2 are correct. The fact that the 1947 data fell on these calculated lines is therefore a check on the validity of the lines of CO Conv. and CO to CO_2 which were established by the data


% H2 to H2O
H2 Conversion
Calc. H2/CO in FF = 1.0
Calc. H2/CO in FF = 2.0

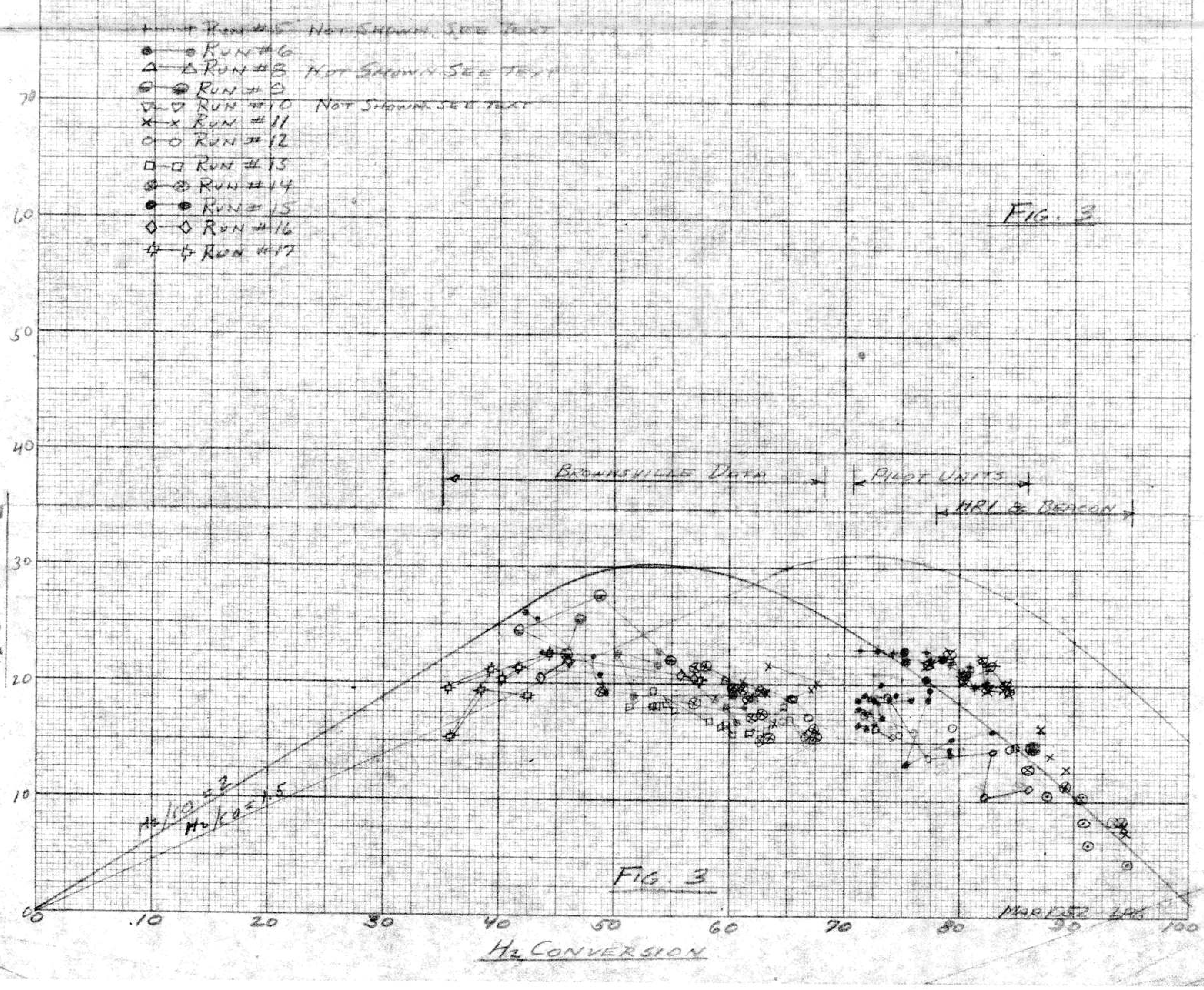

Run #5 Not Shown, See Text
Run #6
Run #8 Not Shown See Text
Run #9
Run #10 Not Shown, See Text
Run #11
Run #12
Run #13
Run #14
Run #15
Run #16
Run #17
Brownsville Data
Pilot Units
HRI & Beacon
% CO to CO2
H2/CO = 2
H2/CO = 1.5
H2 Conversion
Mar 1952

FIG. 3

themselves.

The fact that the present data falls on this same H_2O line while it falls below the CO_2 line in Fig. 3 and the CO line in Fig. 2 shows that the speed of the water gas shift reaction with respect to that of the Fischer-Tropsch reaction is less at Brownsville, Montebello and Stanolind on Mill Scale than it was in the HRI H-Series reactor and in Beacon's runs on CM&S catalyst which runs formed the basis predominantly for the 1947 correlation.

Mill Scale may have exactly the same effect on the Beacon reactors but there, where conversions are so high, the effect is too small to detect.