

Fig. III compares all the Beacon data with the correlation of H₂ Conversion vs. CO in FF to CO₂. It will be noted that:

1. The runs with reduced CM&S catalyst are a good check on the relationship established from HRI data.
2. Adding CO₂ to the feed materially reduces the amount of new CO₂ formed somewhat in proportion to the CO₂ added. If H₂ Conversion were increased by increasing temperature, recycling or catalyst activity, some net disappearance of the CO₂ added could be effected. This however at the expense of some reduction in CO Conversion as shown in Fig. 2.

There is some indication, in Run 22, that CO₂ formation and H₂ formation decrease with catalyst age.

3. The selective qualities of Limonite catalysts are evident here as well as in Figs. I and II. The K₂O produces much more CO₂ than the KF. This may account for the higher CO Conversion and lower H₂ Conversion with the K₂O.

4. The unreduced CM&S catalyst also has a selective effect which changes somewhat with catalyst age. In general it produces less CO₂ which is consistent with the lower CO Conversion experienced at a given H₂ Conversion. The latter is of course considerably lower than was obtained at the same conditions with reduced catalyst.

On Fig. III there are also plotted the Stanolind data for a fresh feed of high H₂/CO ratio and high CO₂ content (CO₂/CO = 35 to 55). It is evident that the CO₂ disappears very rapidly as H₂ disappearance increases.

H₂ Conversion vs. CO to C₃+

Having established the actual CO₂ yield for a given H₂ or CO Conversion, we can calculate by carbon balance what the maximum possible total yield of Hydrocarbons and oxygenated compounds could be, expressed as % CO in the fresh feed as follows: (Assuming of course, that no CO₂ or CH₄ in the fresh feed was converted).

For H₂/CO in FF = 1:

<u>H₂ Conv.</u>	<u>% CO Unconv.</u> (Fig. II)	<u>% CO to CO₂</u> (Fig. III)	<u>% CO to HCs & Oxy. Comps.</u>
25	75	6	19
50	50	13.5	36.5
60	40	17.0	43.0
75	25	23.6	51.4
90	10	32.0	58.0
100	0	39.0	61.0

For H_2/CO in FF = 2.0:

<u>H₂ Conv.</u>	<u>% CO Unconv.</u> (Fig. II)	<u>%CO to CO₂</u> (Fig. III)	<u>% CO to HC_s</u> & Oxy. Comps.
25	50	15.6	34.4
50	7.5	30.2	62.3
60	3.3	29.4	67.3
75	0.5	23.0	76.5
90	0.3	12.2	88.5
100	0	2.5	97.5

The yield of C_3+ for the recalculated HRI data and the Beacon results with CM&S reduced catalyst are compared with the above mathematical results of total HC yield for a 2/1 feed (dotted line) on Fig. IV. If the data can be presumed correct, then the deviation of any point from the dotted line shows the magnitude of the $C_1 + C_2S$ yield. It will be noted that:

1. The reported yield in Run H₆ is much higher than that mathematically possible even when the conversion of some of the CO_2 in the Fresh Feed is accounted for.
2. When the H_2 Conversion is above 85%, contraction over 80%, the yield of C_3+ can vary appreciably even though there is no net disappearance of CO_2 . Since the points in question correlated well on the CO_2 yield and CO conversion relationships, it must be concluded that if the data are correct, certain conditions tend to produce more hydrocarbon gas ($C_1 + C_2S$) than others. It appears that the gas production was highest in the Beacon runs (no CO_2 or CH_4 in FF), lower in H Runs 2, 3, 5A and 5B (no CO_2 but some CH_4 in FF) and lowest in H Runs 17, 24 and 25 (considerable CO_2 and some CH_4 in FF). This indicates that adding CO_2 or CH_4 in the FF can reduce gas yields. On the other hand this effect could well be caused by a combination of other factors and no conclusions should be drawn at this point. The solid line shown can be used only for a rough approximation of the C_3+ yield.

Fig. IVA is a plot of C_3+ yield for all the HRI data taken directly from the HRI summaries. The solid line is that reproduced from Fig. IV. The C_3+ yields obtained in the 14 Series runs 7, 8 and 9 were all considerably lower than those obtained in the H Series.

Fig. IVB is a plot of the C_3+ yield for the Laboratory A data (Low H_2/CO ratio feed.) compared with the calculated maximum and the line

for the 2/1 feed. Here again the scatter is very great but the deviation in this case is apparently due to error or a combination of several factors because no consistent parameter could be found. The solid line through the data is intended for rough approximation purposes only.

Fig. IVC shows all the Beacon data other than that obtained with CM&S reduced catalyst. It will be evident that:

1. Adding CO_2 to the feed increase C_3+ yield.
2. The C_3+ yield with unreduced catalyst at 1/1 recycle ratio was about the same as that obtained with reduced catalyst running once through.
3. The C_3+ yields with the Limonite and other special catalysts was less than that obtained with CM&S reduced catalyst except perhaps for Beacon catalyst #3 which produced a little higher yield than the CM&S catalyst.

H_2 Conversion vs. CO to $\text{C}_1 + \text{C}_2\text{S}$

Fig. V is a plot of the yield of hydrocarbon gas ($\text{C}_1 + \text{C}_2\text{S}$) for all the HRI recalculated data and the Beacon results obtained with CM&S reduced catalyst.

The dotted line is that calculated by Carbon balance assuming that the previously established relationships including the solid line through the data for C_3+ yield were correct. It will be evident that the wide deviation from any average line is more or less in line with previous comments.

Fig. VA is a similar plot of the Laboratory A data. (H_2/CO in $\text{FF} = 1.0$).

It will be clear that in order to prevent the calculated lines on either of these plots from going through a reversal at high conversions as shown, it would be necessary to materially taper off the straight lines for C_3+ yield, reduce the CO_2 yield or increase the % CO converted, none of which are justified by the data. It is indicated therefore that the yield of CH_4 and C_2S may at first increase as H_2 conversion increases and then become less as degree of conversion is further improved.

H₂ Conversion vs. CO to CH₄

The methane yield for the HRI data are plotted on Fig. VIA.

These indicate that methane yield goes through a reversal and increases with recycle ratio.

It appears also from this plot, that adding CH₄ and CO₂ to the fresh feed will reduce the amount of CH₄ made. This is notable in Run 6 where both CH₄ and CO₂ in the fresh feed were high.

Fig. VI is a plot of the methane yield for all the Beacon data, with the lines of Fig. VIA shown dotted. This plot confirms the effect of recycle ratio on methane yield indicated by the HRI data. It also shows that in those Beacon runs which had no CH₄ or CO₂ in the fresh feed, the methane yield was considerably higher than in the HRI runs where the CH₄/CO in the Fresh Feed ranged from 5 to 12 in all cases and the CO₂/CO varied from 0 to 20. The higher yield of CH₄ in the Beacon runs on the other hand, may be due to temperature which in general was 20 to 50° higher in the Beacon runs.

It will be noted from Fig. VI that in the Beacon runs where CO₂ was added deliberately to the Fresh Feed, the methane yield dropped. It will also be noted from this same figure that certain catalysts promote methane yield whereas, the unreduced CM&S catalyst produced less methane for a given H₂ Conversion.

The methane yield is apparently influenced by all of the following factors:

1. H₂/CO ratio in Fresh Feed
2. CO₂ content of Fresh Feed
3. CH₄ content of Fresh Feed
4. Recycle ratio
5. Type of catalyst
6. Temperature

Item #4, recycle ratio, effects the ratio of CH₄/CO₂ in total feed and also the ratio of CH₄/H₂O in total feed. Changes in these ratios may be responsible for the apparent effect of recycle ratio on methane yield.

The only data available where both CO₂ and CH₄ were missing from the fresh feed are those obtained at Beacon. These are plotted together with all the other Beacon data on Fig. VI.