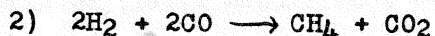


On the other hand the difference may be due to apparatus design and partly to catalyst used. The latter definitely influences the relative rate of CO and H₂ disappearance as we shall see later from the Beacon data.

On this plot there are shown as dotted lines, the relationship between H₂ Conversion and CO Conversion if the following equations occurred.



The data indicate that at first, the H₂ and CO disappear in the ratio of 1/1 and equation (2) most nearly represents what actually occurs at the beginning when the ratio of H₂/CO in the fresh feed is 2/1.

Fig. II shows all the Beacon data (also H₂/CO in FF = 2.0) compared with the H Series line of Fig. IIA. The data with the CM&S reduced catalyst are an excellent check on the HRI H Series data.

It will be noted also that adding CO₂ to the feed definitely lowers the CO Conversion for a given H₂ Conversion. There is no consistent relationship between the magnitude of this effect and the amount of CO₂ added. It appears that a small amount of CO₂ (10% of Fresh Feed) has essentially as much an effect as a large amount of CO₂ (30% of Fresh Feed).

This bears out the previous suggestion that the 14 Series data shown on Fig. IIA may be low partly because the CO₂ content of the Fresh Feed was about 6%.

From this plot it will be noted that:

1. As previous mentioned, CO Conversion alone is not a good measure of catalyst activity or of the effect of operating variables. CO Conversion is always relatively high and not materially effected by temperature or recycle rate. Whereas both of these have a profound effect on H₂ Conversion and % Contraction.

Even with mild conditions or a mild catalyst, the CO practically all disappears, but much of it goes to CO₂. More drastic conditions increase CO Conversion a little but their principal effect is to reduce the CO₂ initially formed with further disappearance of H₂. Therefore, H₂ Conversion or % Contraction is a better indication of degree of conversion.

2. Adding CO_2 to the feed reduces CO Conversion but does not materially affect H_2 Conversion.

3. Recycling 1/1 with unreduced catalyst results in an H_2 conversion little better than that obtained once through with reduced catalyst and the CO conversion is a little less. There is no consistent indication that the catalyst would eventually have conditioned itself to give the same results as obtained with the reduced catalyst in Runs 24 and 27.

4. The results with both limonite catalysts were very poor but there is some indication that the additives have some selective qualities. The KF gives a lower CO disappearance and higher H_2 disappearance than the K_2O .

Fig. IIB is a plot of the H_2 Conversion vs. CO Conversion of all the data from the laboratories A & B. Most of the data from Laboratory A were obtained with a Fresh Feed having an H_2/CO ratio of 1 and a CO_2 content of less than 1%. These particular data are denoted by open squares and it will be noted that, although the scattering is fairly great, they correlate reasonably well on a straight 45° line indicating that in this case H_2 disappears just as fast as CO as would be expected with an equation such as equation (2) above, viz; $\text{H}_2 + \text{CO} \longrightarrow 1/2 \text{CH}_4 + 1/2 \text{CO}_2$.

Some of the data from Laboratory B were obtained with a fresh feed having an H_2/CO ratio of 2 but the CO_2 content in these runs was 7.5 to 8.5% ($\text{CO}_2/\text{CO} = 25$ to 30) and the CO Conversion was considerably less than those in the HRI and Beacon 2/1 runs, the line for which is shown on Fig. IIB for comparison.

The runs from Laboratory A with 1.5 H_2/CO ratio in the Fresh Feed fall about where expected. In these the CO_2 content of the feed was low. Many of those of Laboratory B however, where the CO_2 content varied from 13 to 19% ($\text{CO}_2/\text{CO} = 35$ to 55%) show low CO Conversions. The line for $\text{H}_2/\text{CO} = 1.5$ and CO_2 in FF = 0 is approximate only.

Fig. IIC shows the H_2 Conversion vs. CO Conversion of the Stanolind data. The solid line on this figure is that for H_2/CO in FF = 2 reproduced from Fig. IIB and the dotted line is that calculated for 4/1 ratio assuming that at the beginning, CO and H_2 disappeared on a 1/1 basis the same as they

apparently do when the fresh feed H_2/CO is 1/1 or 2/1.

The Stanolind fresh feed always contained 7 to 10% CO_2 ($CO_2/CO = 35$ to 55%) and considerable CH_4 . The H_2/CO ratio was 4 or more in all except three runs. In two of these it was 2.3 as noted. These two runs fall more or less where expected. In the other runs however, the H_2 disappearance was considerably greater than expected. Some of the surplus H_2 was used up in reaction with the CO_2 to produce Hydrocarbons and H_2O .

Probably for all of these data a better correlation could be obtained if $CO + CO_2$ Conversion were plotted instead of CO Conversion.

H_2 Conversion vs. CO in FF to CO_2

Fig. IIIA shows H_2 Conversion vs. CO to CO_2 for all the HRI data. The data may be divided into three groups:

- A. H_2/CO in FF = 2, % CO_2 in FF = 0
H Runs 5B, 14 and 17
- B. H_2/CO in FF = 2, % CO_2 in FF = 4-6
Five of the calculated H Series runs and all the 14 Series runs.
- C. H_2/CO in FF = 2.2-2.5, % CO_2 in FF = 0
The remainder of the H Series runs.

These data and those from other laboratories to be submitted below indicate that both H_2/CO ratio in FF and CO_2 content of FF effect CO_2 yield for a given degree of conversion. Therefore three lines have been shown as noted.

It is possible that a more careful analysis of the 14 Series data, which scatter badly, would show the effects of other variables on CO_2 yield but time did not permit such a study at this time.

It will be noted that CO_2 yield definitely goes through a maximum and after the H_2 Conversion exceeds 50 to 55%, it decreases as conversion increases.

Fig. IIIB shows the data of Laboratory B Runs 11 and 12 which were made with a fresh feed having an H_2/CO ratio of 2.0 with a CO_2 content of 7 to 8% (CO_2/CO in FF = 25-30). All but one point fit reasonably well on a single curve drawn through the only point available at Beacon and HRI Run H 6 with approximately the same CO_2 content in the Fresh Feed.

Fig. IIIC is a plot of all the data available with the H_2/CO ratio in the Fresh Feed equal to 1.0 (Lab. A). There is a slight indication that CO_2 yield drops off as CH_4 in FF increases but this effect is probably within the accuracy of the data.

Since the shape of this curve is radically different from those for 2/1 feed there was some doubt about the accuracy of the data.

However, if we assume the relationships previously established to be correct it is possible to calculate the maximum possible yield of CO_2 stoichiometrically as follows:

For $H_2/CO = 1.0$

<u>H_2 Conv.</u>	<u>CO Conv. Fig. IIB</u>	<u>% Contr. Fig. IC</u>	<u>Max. Yield CO_2/CO</u>	<u>Limiting Condition</u>
25	25	17	12.5	O ₂ Balance
50	50	37	25.0	O ₂ Balance
75	75	57	36.0	Contraction
100	100	75	50.0	Both

For $H_2/CO = 1.5$

<u>H_2 Conv.</u>	<u>CO Conv. Fig. IIB</u>	<u>% Contr. Fig. IC</u>	<u>Max. CO_2/CO</u>	<u>Limiting Condition</u>
25	37.7	20.1	18.5	O ₂ Balance
50	75.2	42.2	37.5	O ₂ Balance
75	93.3	63.6	46.6	Both
100	100	85.0	37.5	Contraction

For $H_2/CO = 2.0$

<u>H_2 Conv.</u>	<u>CO Conv. Fig. II</u>	<u>% Contr. Fig. IC</u>	<u>Max. CO_2/CO</u>	<u>Limiting Condition</u>
25	50	23.5	25.0	O ₂ Balance
50	92.5	47.2	47.0	O ₂ Balance
75	99.5	71.2	36.0	Contraction
100	100	95	15.0	Contraction

Fig. IIID shows these calculated maxima curves in solid compared with those predicted by the data in dotted.

Fig. IIIE is a plot of all the data available for a fresh feed having an H_2/CO ratio = 1.2 to 1.5. The data from Laboratory A fall where they should but many of those from Laboratory B show a much lower yield of CO_2 than would be expected perhaps because the CO_2 and CH_4 content of the fresh feed was very high. The data of run 5A are obviously in error and are so designated.